

2007

## Accurate Ab Initio Potential Energy Curve of F<sub>2</sub>. III. The Vibration Rotation Spectrum

Laimutis Bytautas  
*Iowa State University*

Nikita Matsunaga  
*Long Island University - Brooklyn Campus*

Takeshi Nagata  
*Iowa State University*

Mark S. Gordon  
*Iowa State University, mgordon@iastate.edu*

Klaus Ruedenberg  
*Iowa State University, klausrg@iastate.edu*

Follow this and additional works at: [http://lib.dr.iastate.edu/chem\\_pubs](http://lib.dr.iastate.edu/chem_pubs)

 Part of the [Chemistry Commons](#)

The complete bibliographic information for this item can be found at [http://lib.dr.iastate.edu/chem\\_pubs/484](http://lib.dr.iastate.edu/chem_pubs/484). For information on how to cite this item, please visit <http://lib.dr.iastate.edu/howtocite.html>.

---

# Accurate Ab Initio Potential Energy Curve of F<sub>2</sub>. III. The Vibration Rotation Spectrum

## Abstract

An analytical expression is found for the accurate *ab initio* potential energy curve of the fluorine molecule that has been determined in the preceding two papers. With it, the vibrational and rotational energy levels of F<sub>2</sub> are calculated using the discrete variable representation. The comparison of this theoretical spectrum with the experimental spectrum, which had been measured earlier using high-resolution electronic spectroscopy, yields a mean absolute deviation of about 5 cm<sup>-1</sup> over the 22 levels. The dissociation energy with respect to the lowest vibrational energy is calculated within 30 cm<sup>-1</sup> of the experimental value of 12953 ± 8 cm<sup>-1</sup>. The reported agreement of the theoretical spectrum and dissociation energy with experiment is contingent upon the inclusion of the effects of core-generated electron correlation, spin-orbit coupling, and scalar relativity. The Dunham analysis [Phys. Rev. 41, 721 (1932)] of the spectrum is found to be very accurate. New values are given for the spectroscopic constants.

## Keywords

Ab initio calculations, Dissociation energies, Polynomials, Dissociation, Electron correlation calculations

## Disciplines

Chemistry

## Comments

The following article appeared in *Journal of Chemical Physics* 127 (2007): 204313, and may be found at doi: [10.1063/1.2805392](https://doi.org/10.1063/1.2805392).

## Rights

Copyright 2007 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

**Accurate ab initio potential energy curve of F 2 . III. The vibration rotation spectrum**

L. Bytautas, N. Matsunaga, T. Nagata, M. S. Gordon, and K. Ruedenberg

Citation: *The Journal of Chemical Physics* **127**, 204313 (2007); doi: 10.1063/1.2805392

View online: <http://dx.doi.org/10.1063/1.2805392>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/127/20?ver=pdfcov>

Published by the [AIP Publishing](#)

---

**Articles you may be interested in**

[Accurate ab initio potential energy surface, thermochemistry, and dynamics of the F<sup>-</sup> + CH<sub>3</sub>F SN<sub>2</sub> and proton-abstraction reactions](#)

*J. Chem. Phys.* **142**, 244301 (2015); 10.1063/1.4922616

[Ab initio potential energy surface and vibration-rotation energy levels of lithium monohydroxide](#)

*J. Chem. Phys.* **138**, 234301 (2013); 10.1063/1.4810864

[Accurate ab initio potential energy curve of O 2 . II. Core-valence correlations, relativistic contributions, and vibration-rotation spectrum](#)

*J. Chem. Phys.* **132**, 074307 (2010); 10.1063/1.3298376

[Accurate ab initio potential energy curve of F 2 . II. Core-valence correlations, relativistic contributions, and long-range interactions](#)

*J. Chem. Phys.* **127**, 204301 (2007); 10.1063/1.2801989

[Spectroscopic constants and potential energy curves of tungsten carbide](#)

*J. Chem. Phys.* **112**, 7425 (2000); 10.1063/1.481373

---



**AIP** | APL Photonics

*APL Photonics* is pleased to announce  
**Benjamin Eggleton** as its Editor-in-Chief



## Accurate *ab initio* potential energy curve of F<sub>2</sub>. III. The vibration rotation spectrum

L. Bytautas

Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA and Ames Laboratory USDOE, Iowa State University, Ames, Iowa 50011, USA

N. Matsunaga

Department of Chemistry and Biochemistry, Long Island University, Brooklyn, New York 11201, USA

T. Nagata, M. S. Gordon, and K. Ruedenberg<sup>a)</sup>

Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA and Ames Laboratory USDOE, Iowa State University, Ames, Iowa 50011, USA

(Received 10 July 2007; accepted 11 October 2007; published online 30 November 2007)

An analytical expression is found for the accurate *ab initio* potential energy curve of the fluorine molecule that has been determined in the preceding two papers. With it, the vibrational and rotational energy levels of F<sub>2</sub> are calculated using the discrete variable representation. The comparison of this theoretical spectrum with the experimental spectrum, which had been measured earlier using high-resolution electronic spectroscopy, yields a mean absolute deviation of about 5 cm<sup>-1</sup> over the 22 levels. The dissociation energy with respect to the lowest vibrational energy is calculated within 30 cm<sup>-1</sup> of the experimental value of 12 953 ± 8 cm<sup>-1</sup>. The reported agreement of the theoretical spectrum and dissociation energy with experiment is contingent upon the inclusion of the effects of core-generated electron correlation, spin-orbit coupling, and scalar relativity. The Dunham analysis [Phys. Rev. **41**, 721 (1932)] of the spectrum is found to be very accurate. New values are given for the spectroscopic constants. © 2007 American Institute of Physics.  
[DOI: 10.1063/1.2805392]

### I. INTRODUCTION

The quantum mechanical *ab initio* calculations in the two preceding papers<sup>1,2</sup> have accounted for all physical interactions that are expected to have a bearing on the potential energy curve for the ground state dissociation of F<sub>2</sub> with an error bar of a few tenths of a millihartree: electronic correlations as well as relativistic effects including spin-orbit coupling. These energies were obtained at 13 internuclear distances along the dissociation curve. In the present investigation, we examine whether this *ab initio* information is adequate to determine the potential energy curve well enough for the calculation of the rotation-vibration spectrum and, if so, how well the resulting spectrum agrees with the known experimental data.

Within the Born-Oppenheimer approximation,<sup>3</sup> the nuclear motion is determined by a potential energy surface<sup>4,5</sup> that is determined through electronic quantum mechanics. While group theory can elucidate certain global features of energy landscapes,<sup>6-9</sup> quantitatively accurate potential energy surfaces are needed in many contexts. Thus, chemical reaction rates<sup>10-15</sup> are sensitive to energy barriers calculated for transition structures, and thermodynamic properties<sup>16,17</sup> depend on the accuracy of the calculated harmonic and anharmonic frequencies.<sup>18</sup> This demand is motivating work on *ab initio* methods capable of yielding the desired accuracy<sup>4,5,19-21</sup> and the search for new methodological

approaches.<sup>22-27</sup> Interest also continues in methods for deducing accurate potential energy functions directly from observed vibrational spectra.<sup>28-30</sup> The best available potential energy curves are also useful in the modeling of “universal” potential energy functions.<sup>31-33</sup> A valuable tool in assessing the quality of theoretical potential energy surfaces is the spectroscopy of diatomic molecules.<sup>34,35</sup>

For a long time, the molecules H<sub>2</sub>,<sup>36</sup> H<sub>2</sub><sup>+</sup>,<sup>37-39</sup> and H<sub>3</sub><sup>+</sup> (Refs. 40 and 41) were the only ones for which *ab initio* calculated potential energy surfaces existed that yielded vibration-rotation levels within 1 cm<sup>-1</sup> of the experimental measurements. In recent years, however, this situation has begun to change. For the LiH<sup>+</sup> ion (three electrons), the lowest five vibrational energy spacings were calculated by Bubin and Adamowicz<sup>42</sup> within 0.1 cm<sup>-1</sup> of the experimental values.<sup>42</sup> For the LiH molecule (four electrons), Bubin *et al.*<sup>43</sup> obtained the 0 → 1 transition energy within 1 cm<sup>-1</sup> of the experimental value. *Ab initio* calculations for the Be<sub>2</sub> molecule (eight electrons) were performed by Martin<sup>44</sup> and by Gdanitz.<sup>45</sup> The former obtained the lowest four vibrational energy spacings, the only ones observed experimentally, with a mean absolute deviation (MAD) of 9.1 cm<sup>-1</sup>, the latter with a MAD of 4.9 cm<sup>-1</sup>. Gdanitz<sup>45</sup> also calculated seven additional levels.

Potential energy surfaces for the ten-electron systems HF and H<sub>2</sub>O have also been reported. For the latter, Polyansky *et al.*<sup>46</sup> calculated the vibrational band origins. They list 12 of them explicitly and report standard deviations from the experimental values averaging over all 104 observed band

<sup>a)</sup>Electronic mail: ruedenberg@iastate.edu

origins, obtaining a value of  $7.9\text{ cm}^{-1}$  for the nonrelativistic calculation, of  $4.2\text{ cm}^{-1}$  after inclusion of relativistic corrections, and of  $1.9\text{ cm}^{-1}$  after further inclusion of quantum electrodynamic and Born-Oppenheimer diagonal correction effects. The HF molecule has been treated in several studies.<sup>47–50</sup> The best of these, by Cardoen and Gdanitz,<sup>50</sup> includes core correlations and relativistic effects. The mean absolute deviation is  $21\text{ cm}^{-1}$  for the 19 vibrational energy transitions from the lowest level, the maximum deviation from experiment of  $77\text{ cm}^{-1}$  occurring for the highest level,  $v=19$ .

Other *ab initio* calculations of diatomic molecules with two heavy nuclei<sup>51–57</sup> have come less close to the experimental spectra. Laidig *et al.*<sup>51</sup> performed one of the earliest *ab initio* studies of the vibrational levels of  $\text{N}_2$  and  $\text{F}_2$ . They calculated the vibrational energy spacings of the lowest five levels using a multireference (MR) linearized coupled-cluster method and a basis set of “better than” double zeta plus polarization quality. The errors in the vibrational level spacings of  $\text{N}_2$  vary from  $72$  to  $75\text{ cm}^{-1}$ , and those for  $\text{F}_2$  vary from  $83$  to  $111\text{ cm}^{-1}$ . Li and Paldus<sup>52</sup> have calculated the  $\text{N}_2$  potential energy curve using their eight-reference reduced multireference (RMR) method with a cc-pVTZ basis, not including correlating core electrons and relativity effects. The vibrational levels they calculated yield errors of  $\sim 100\text{ cm}^{-1}$  for  $v=19$ , which is surprisingly close considering the smallness of the basis set and the approximations used. Recent work of Nooijen and Le Roy<sup>53</sup> reports potential energy curves and spectroscopic constants for  $\text{N}_2$  and  $\text{O}_2$  derived from up to eight low lying vibrational energy levels. Here, as in the work of Laidig *et al.*,<sup>51</sup> the use of the small cc-pVDZ basis stands in the way of a realistic vibrational spectrum. The best *ab initio* potential energy values for the  $\text{N}_2$  molecule are those of Gdanitz<sup>54</sup> based on the  $r_{12}$ -MR-ACPF method with an *spdfgh* basis, including core correlation but no relativistic effects. Using novel functional forms for the potential energy curve, Le Roy *et al.*<sup>30</sup> have deduced an analytical potential energy curve from Gdanitz’ *ab initio* data,<sup>54</sup> calculated the vibrational spectrum, and compared it with the spectrum obtained from a near-exact potential derived from the spectroscopic data (the “recommended experimental potential” of Ref. 30). They<sup>30</sup> found vibrational level deviations ranging from  $35\text{ cm}^{-1}$  for  $v=19$  up to  $\sim 210\text{ cm}^{-1}$  for higher  $v$ .

One has to infer that the attainment of a MAD of  $20\text{ cm}^{-1}$  or less for the vibrational levels of diatomic molecules with two heavy nuclei places high demands on the level of theory regarding the recovery of correlation, the quality of the basis sets, and the necessity of considering core effects and relativistic corrections.

For the  $\text{F}_2$  molecule, containing two heavy nuclei and 18 electrons, very accurate calculations have so far only been made in a limited region around the equilibrium distance, where the coupled-cluster methodology is effective. From this local part of the potential energy curve, the spectroscopic constants  $R_e$  and  $\omega_e$  are then determined. Thus, Ruden *et al.*<sup>58</sup> reported accurate *ab initio* values for  $R_e$  and  $\omega_e$ , and Heckert *et al.*<sup>59</sup> reported an accurate  $R_e$  value. These calculations offer an improvement over other, mostly earlier

results.<sup>60–68</sup> Additional spectroscopic constants have been calculated by *ab initio* means by various authors<sup>69–75</sup> employing relatively large basis sets and reasonably high levels of theory, with and without core correlations, but without relativistic corrections. Earlier work is based on relatively small basis sets.<sup>76</sup> A comprehensive review of theoretically predicted spectroscopic constants of  $\text{F}_2$  was given by Pittner *et al.*<sup>77</sup>

There also exists an *ab initio* study<sup>78</sup> of vibrational levels in three electronically *excited* singlet states of  $\text{F}_2$  (5 levels in two  $\Pi$  states and  $\sim 30$  levels in a  $\Sigma$  state). Here, the deviations of the calculated harmonic frequencies from the experimental data range from  $\sim 100$  to  $\sim 700\text{ cm}^{-1}$ .

A considerable number of *ab initio* investigations of the  $\text{F}_2$  molecule focus on method development.<sup>79–93</sup> In this context, the comparison to full configuration interaction (CI) benchmarks is relevant which automatically limits the size of usable basis sets. Thus, even though the full dissociation curve may be calculated, no attempts are made to determine the spectrum.

So far only the lowest ( $\leq 5$ ) vibrational levels of the  $1\Sigma_g^+$  ground state of  $\text{F}_2$  have been calculated.<sup>51,55–57</sup> The  $0 \rightarrow 1$  transition energy was obtained within  $1.7\text{ cm}^{-1}$  in Ref. 55 and within  $48.8\text{ cm}^{-1}$  in Ref. 57. As yet, no attempt has been made to obtain the full potential energy curve with an accuracy that would warrant calculating the full vibration rotation spectrum (see also the Note added in proof).

In the present investigation, we use the potential energy curve determined in the preceding two papers<sup>1,2</sup> to calculate the dissociation energy as well as the full vibration rotation spectrum. The dissociation energy has recently been determined by Yang *et al.*<sup>94</sup> using ion-pair dissociation imaging. The vibration rotation spectrum had been measured in 1976 at the Herzberg Institute in Ottawa by means of high-resolution electronic spectroscopy.<sup>95</sup> The mean absolute deviation between the 22 experimentally observed and our *ab initio* calculated levels turns out to be  $5\text{--}6\text{ cm}^{-1}$ .

We are using the conversion factor:  $1\text{ mhartree} \equiv 219.4746\text{ cm}^{-1}$ .

## II. ANALYTICAL EXPRESSION OF THE POTENTIAL ENERGY CURVE

In order to be able to solve the Schrödinger equation for the vibration-rotation spectrum numerically, we must be able to calculate the molecular energies at arbitrary points along the dissociation path. Numerous formulas have been developed since the earliest days of quantum mechanics for the representation of diatomic potential energy curves. Good recent discussions of this subject are given in the book by Ogilvie<sup>35</sup> and in several reviews.<sup>96</sup> Recent developments can be found in Refs. 30, 47, 49, and 50. In the context of the present work, we felt that it would be most effective if we could find an analytical expression that would cover the entire range and still be sufficiently flexible to represent *accurately* all 13 *ab initio* calculated energies of Table IV of the preceding paper.<sup>2</sup>

TABLE I. Parameters of analytical even-tempered Gaussian expansions [Eq. (1b)] for the ground state potential energy curve of F<sub>2</sub>. Units:  $\alpha$  in Å<sup>-2</sup>,  $\beta$  is dimensionless, and  $a_k$  in hartree.

Variants <sup>a</sup>	$\alpha$	$\beta$	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$
EXTR1c <sup>b</sup>	0.82	1.55	-0.178 816 962 7	-1.516 939 121 0	5.062 141 563 4	-2.943 934 658 0	16.719 611 821
EXTR2c <sup>c</sup>	0.82	1.55	-0.178 699 088 5	-1.527 611 021 6	5.124 452 104 4	-3.178 358 599 5	17.471 918 762
EXTR3c <sup>d</sup>	0.85	1.52	-0.224 149 377 4	-1.530 938 098 1	5.178 362 024 5	-3.154 904 182 6	14.696 986 169
EXTR4c <sup>e</sup>	0.83	1.53	-0.184 678 669 9	-1.550 622 572 9	4.977 394 544 0	-2.799 944 461 9	14.614 729 739
EXTR5c <sup>f</sup>	0.93	1.49	-0.438 115 197 5	-1.321 334 613 7	6.245 777 341 8	-5.971 316 876 4	19.524 853 248
EXTR4/CBS <sup>g</sup>	0.66	1.78	-0.095 914 365 4	-1.082 024 487 0	4.366 269 647 5	-0.769 245 026 4	63.648 538 690
EXTR4/CBS+CV <sup>h</sup>	0.68	1.75	-0.108 428 762 3	-1.091 468 634 9	4.307 314 929 3	-0.598 866 796 3	48.560 315 466
EXTR4/ CBS+CV+SO <sup>i</sup>	0.83	1.53	-0.184 331 888 2	-1.549 886 896 3	4.967 871 134 6	-2.792 921 379 9	14.645 247 623
RKR <sup>j</sup>	0.41	2.36	0.005 331 26	-0.758 546	4.467 76	-8.127 92	233 913.562 01
Empirical	0.60	1.79	-0.009 150 59	-1.112 750 5	3.233 256 87	2.248 883 98	23.096 214 97

<sup>a</sup>The first eight variants results from least mean squares fits to various *theoretical* energy sets for  $V(R)$ ; see text. Footnotes (b)–(i) list the root-mean-square deviation  $\Delta$  from the respective theoretical data for each of these fits. The variant in the last row, on the other hand, most closely reproduces the *experimental spectrum* (Ref. 95); see text.

<sup>b</sup> $\Delta=0.065$  mhartree.

<sup>c</sup> $\Delta=0.050$  mhartree.

<sup>d</sup> $\Delta=0.068$  mhartree.

<sup>e</sup> $\Delta=0.057$  mhartree.

<sup>f</sup> $\Delta=0.056$  mhartree.

<sup>g</sup> $\Delta=0.087$  mhartree.

<sup>h</sup> $\Delta=0.086$  mhartree.

<sup>i</sup> $\Delta=0.057$  mhartree.

<sup>j</sup>Even-tempered fit to 46 RKR data points of Ref. 95 with the root-mean-square deviation of  $\Delta=0.2280$  mhartree.

## A. Even-tempered representation

For more than a quarter of a century, the *even-tempered exponential and Gaussian expansions*<sup>97–99</sup> have proven to be a remarkably flexible as well as effective tool for the construction of the radial parts of atomic basis orbitals in many contexts. They are defined as

$$f(R) = \sum_k a_k \exp(-\alpha\beta^k R), \quad k=0,1,2,\dots,K, \quad (1a)$$

$$g(R) = \sum_k a_k \exp(-\alpha\beta^k R^2), \quad k=0,1,2,\dots,K, \quad (1b)$$

respectively. The geometric-series-type exponent sequence  $\alpha\beta^k$  not only reduces the nonlinear parameter fitting to an easily manageable task but, equally importantly, also greatly delays the onset of linear dependence with increasing expansion basis size. This is because one readily verifies that

$$\langle g_k | g_{k+1} \rangle [\langle g_k | g_k \rangle \langle g_{k+1} | g_{k+1} \rangle]^{-1/2}$$

is a function of  $\beta$  only and not a function of  $k$ ,

where  $g_k$  denotes any one of the expansion functions in the expressions of Eq. (1). This implies that the  $g_k$  are “evently distributed” over the function space they span. On the other hand, notwithstanding the simple form of the exponent sequence, expansions of the form (1) have proven extremely flexible and they can also readily express functions that have an arbitrary number of maxima and minima.

We have now found that such expansion bases also offer a practical vehicle for the representation of a diatomic potential energy curve as a function of the internuclear distance. In view of the near-Gaussian decay found in Sec. III A of the preceding paper<sup>2</sup> for the F<sub>2</sub> dissociation curve between 1.6 and 2.8 Å, we chose here the expansion (1b) in terms of

even-tempered Gaussian functions. In other systems, the exponential alternative may be more appropriate.<sup>100,101</sup> We determined the parameters by least mean squares fitting to the 13 data points provided by the energies in the last column of Table IV of the preceding paper.<sup>2</sup> The coefficients  $a_k$  were obtained by linear regression, the fit being forced to go to zero at 1000 Å. The exponent parameters  $\alpha$  and  $\beta$  were then obtained by nonlinear minimization. Analogous fits were determined for the alternative potentials referred to in Sec. III A of the preceding paper.<sup>2</sup>

Successively increasing the number of terms, we found that the fits improved up to  $K=4$ . The curvature of each fit changes sign only at one internuclear distance (viz., the inflection point on the dissociation curve), which shows that the small scatterings in the data due to inaccuracies were not fitted. In all cases, the root-mean-square deviation was between 0.05 and 0.09 mhartree, which is better than the surmised accuracy of the *ab initio* calculations (about 0.2 mhartree). On the other hand, a six-term expansion (i.e.,  $K=5$ ) yielded minimal further lowering of the Least-Mean-Square (LMSQ) deviation, while introducing very large successive expansion coefficients with alternating signs.

The resulting even-tempered expansions are listed in Table I. The first row, labeled EXTR1c, contains the expansion parameters for the potential energy curve in the last column of Table IV of the preceding paper.<sup>2</sup> As discussed in the last paragraph of Sec. III A of that paper, we also considered four slightly modified energy curves, labeled EXTR2c, EXTR3c, EXTR4c, and EXTR5c, which resulted from slight variations in the correlation energy extrapolation by intrinsic scaling (CEEIS) extrapolation.<sup>1</sup> The expansion parameters of these potential energy curves are given in rows 2–5 of Table I.

In order to be able to assess the importance of the *individual* correction terms that were calculated in Sec. II of the preceding paper,<sup>2</sup> we furthermore determined the analytical expressions for the potential energy curves that contain none or only some of these corrections. In this context, we used only the curve EXTR4. The resulting parameters are given in rows 6–8, specifically as follows.

- (1) The sixth row of Table I, labeled EXTR4/CBS, represents the dissociation curve containing only nonrelativistic valence shell correlations.
- (2) The seventh row, labeled EXTR4/CBS+CV, represents the dissociation curve containing the correlation of *all* electrons.
- (3) The eighth row, labeled EXTR4/CBS+CV+SO, represents the dissociation curve containing all correlations as well as spin-orbit coupling.
- (4) Final addition of the scalar relativistic terms brings us back to the fourth row EXTR4c.

The analytic representations of this table will be used in the rotational-vibrational Schrödinger equation.

## B. Long-range and short-range adjustments

The preceding analytical expressions presume that no solid information is available about the manner in which the potential energy curve decays beyond the last known energy value. Note, for instance, the complicating influences on the long-range behavior of the dissociation curve of F<sub>2</sub>, which were discussed in Sec. IV of the preceding paper.<sup>2</sup> It is, however, a fact that all our nonrelativistic analytical potentials yield vibrational spectra whose highest levels tend to lie too high, which appears to imply that the Gaussian decay is eventually too steep. We also noted in Sec. IV of the preceding paper that relativistic corrections and higher-order correlation terms soften the long-range decay, which may lead one to speculate that the latter may impart an inverse power dependence to the long-range part of the potential.

Such knowledge regarding the long-range decay, if it exists, can be incorporated in the analytic expressions of the preceding section as follows.

Suppose that, at long range, the potential energy curve has the general form

$$V_{LR}(R) = A \times L(R), \quad (2)$$

where  $L(R)$  defines the specific functional dependence, e.g.,  $A \times L(R) = A \times (R^{-5} + bR^{-6} + cR^{-7} + \dots)$ . The modified potential energy curve is then taken as follows:

$$\text{for } 0 \leq R \leq R_0: \quad W(R) = V(R),$$

the potential determined above,

$$\text{for } R_0 \leq R \leq R_1: \quad W(R) = S(R) \times V(R),$$

a transition splice,

$$\text{for } R_1 \leq R \leq \infty: \quad W(R) = A \times L(R),$$

the long-range potential, (3a)

where the splice factor is

$$S(R) = (1 + k\rho^3) \quad \text{with } \rho = R - R_0. \quad (3b)$$

By construction, the potential  $W(R)$  as well as its first and second derivatives are continuous at the point  $R=R_0$ . We furthermore require that  $W(R)$  and its first and second derivatives are also continuous at the point  $R=R_1$ . After some algebra, these requirements yield the three equations

$$SV = A \times L, \quad (4)$$

$$[V' + (3/\rho)V]S - (3/\rho)V = A \times L', \quad (5)$$

$$[V'' + (6/\rho)V' + (6/\rho^2)V]S - (6/\rho)V' - (6/\rho^2)V = A \times L'', \quad (6)$$

where  $V, V', V'', L, L',$  and  $L''$  are meant to denote the values of these functions and derivatives at the point  $R_1$ . Equations (4)–(6) determine the parameters  $R_0, R_1,$  and  $k,$  which specify the splice, as functions of  $A.$  Hence, an additional condition can be satisfied, for instance, that  $A$  has a specific value or that some property of energy spectrum is matched.

The relationship between  $R_0, R_1, k,$  and  $A$  can be made explicit as follows. One can consider Eqs. (4)–(6) as a set of homogeneous linear equations for the three nonzero quantities  $\{S, A, 1\}.$  This implies that the  $3 \times 3$  determinant of the respective coefficients must vanish. After some algebra, this condition yields the following equation for  $\rho:$

$$\rho = \left\{ \left[ \frac{1}{2}(LV'' - VL'')/(LV' - VL') \right] - (V'/V) \right\}^{-1}. \quad (7)$$

If one assumes a value for  $R_1,$  then Eq. (7) allows the calculation of  $\rho = (R_1 - R_0)$  from the values of  $V, V', V'', L, L',$  and  $L''$  at the point  $R_1.$  Hence the value of  $R_0$  is also known. Furthermore, after inserting the value of  $\rho$  into Eqs. (3b) and (5), the three equations, Eqs. (3b), (4), and (5), are readily solved for the three quantities  $A, k,$  and  $S(R_1)$  by successive substitutions. The algorithm easily yields  $(R_0, k, A)$  as numerical functions of  $R_1$  as well as the inverse numerical relations.

This splicing procedure can also be used at very short distances if the functional form of the *increasing* potential in that region is known.

## C. An optimal empirical potential energy curve

How close are the *ab initio* potential energy curves of Sec. II A to an empirical curve that yields the experimental levels with spectroscopic accuracy?

Our first attempt at finding such an empirical potential consisted of fitting an even-tempered expansion to the RKR (see Ref. 28) curve given by Colbourn *et al.*<sup>95</sup> Its expansion coefficients are listed in the second to last row of Table I. Using the method to be discussed in Sec. III A, we obtained from it a theoretical vibrational spectrum with a mean absolute deviation of 1.95 cm<sup>-1</sup> from the experimental spectrum, provided we omitted the highest level ( $v=22$ ), which deviated by 18.4 cm<sup>-1</sup>.

Guided by our *ab initio* results, we were able to construct a better empirical even-tempered potential energy curve that yielded a vibrational spectrum with a mean absolute deviation of 0.88 cm<sup>-1</sup> from the experimental spectrum,

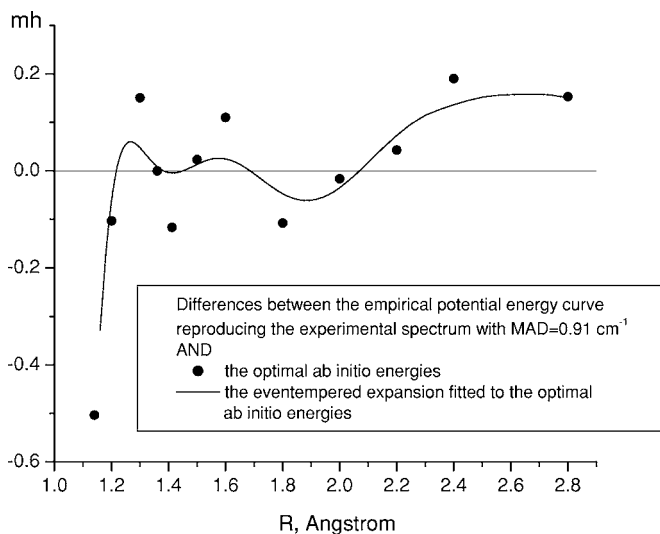


FIG. 1. Deviation of *ab initio* energies (in mhartree) and their analytical fit (EXTR4c) from an empirical potential energy curve  $W(R)$  that yields the experimental vibrational spectrum with a mean absolute deviation of  $0.91 \text{ cm}^{-1}$ .

when we excluded the highest level ( $v=22$ ), which deviated by  $12 \text{ cm}^{-1}$ . The coefficients of this expansion are listed in the last row of Table I. Note also that, here, the coefficient  $a_4$  has a very reasonable value as compared to the excessive value of 234 000 required for the RKR fit.

Since the level for  $v=22$  was too high by  $12 \text{ cm}^{-1}$ , we corrected this empirical expansion by adding a long-range splice of the type discussed in the preceding section. In view of the relation to electron correlation, noted in Sec. IV of the preceding paper,<sup>2</sup> we assumed for  $L(R)$  in Eq. (2) the form  $R^{-6}$ . As noted in the preceding section, this type of composite potential  $W(R)$  still has one degree of freedom. We chose this remaining variable as the mean absolute deviation of the vibrational levels  $v=20, 21, 22$  from experiment and found that it had a sharp minimum of  $1 \text{ cm}^{-1}$  for the splice parameter values

$$\begin{aligned} R_0 &= 2.4294 \text{ \AA}, & R_1 &= 2.9890 \text{ \AA}, \\ k &= 9.7447 \text{ hartree \AA}^{-3}, \\ A &= -0.22899 \text{ hartree \AA}^6 = -10.4282 \text{ hartree bohr}^6. \end{aligned} \quad (8)$$

(Parenthetically, we note that the  $A$  value differs only by 10% from the value of  $C_6$  calculated by Chu and Dalgarno<sup>102</sup> see also Sec. IV B of the preceding paper.<sup>2</sup>)

The composite potential energy curve  $W(R)$  of Eq. (3a) yields then a vibrational spectrum with a mean absolute deviation of  $0.91 \text{ cm}^{-1}$  from experiment, where now all 22 levels are included.

A comparison between this empirical composite analytical potential energy curve and the *ab initio* energies of the curve EXTR4c is presented in Fig. 1, as follows.

- As solid dots: the differences between the 12 *ab initio* energy values and the corresponding values on the empirical curve  $W(R)$ .
- As solid line: the difference between the *ab initio* fitted

analytical curve and the analytical empirical curve  $W(R)$ .

The actually calculated *ab initio* energies (dots) are seen to scatter fairly evenly around the empirical curve with a mean absolute deviation of  $27.8 \text{ cm}^{-1}$ , which is somewhat less than the possible error of  $65 \text{ cm}^{-1}$  estimated in the first paper of this series.<sup>1</sup> The maximum deviation in the range between 1.16 and  $2.8 \text{ \AA}$ , where all energy levels lie, is  $44 \text{ cm}^{-1}$ . Due to this fairly even scatter, the even-tempered fit to EXTR4c is on the average much closer to the empirical analytical curve  $W(R)$  than the individual *ab initio* points, the mean absolute deviation between these two curves being  $13.2 \text{ cm}^{-1}$ .

### III. DETERMINATION OF THE ROTATION-VIBRATION SPECTRUM

#### A. Solution of eigenvalue equation

The calculation of the rotational and vibrational energy levels  $E_{v,J}$  for F<sub>2</sub>, where  $v$  and  $J$  are the vibrational and rotational quantum numbers, respectively, requires the solution of the eigenvalue problem of the nuclear Schrödinger equation<sup>103</sup>

$$\begin{aligned} -(\hbar^2/2\mu)\partial^2 f(R)/\partial R^2 + [(\hbar^2/2\mu)J(J+1)/R^2 + V(R)]f(R) \\ = E_{v,J}f(R), \end{aligned} \quad (9)$$

where  $R$  is the internuclear distance,  $V(R)$  is one of the potential energy functions constructed in Sec. II A, and

$$f(R) = R \times \psi(R), \quad (10)$$

with  $\psi(R)$  being the radial part of the wavefunction after factoring off the spherical harmonics containing the angular coordinates. According to the NIST Database,<sup>104</sup> the value of the reduced mass  $\mu$  of the two fluorine nuclei is  $\frac{1}{2}18.998\,403\,2 \text{ amu}$ .

To solve Eq. (9), we have used the discrete variable representation of Light and co-workers<sup>105,106</sup> in the form it has been cast by Colbert and Miller.<sup>107</sup> These authors showed that the kinetic energy matrix in this representation can be chosen as

$$T_{ij} = [\hbar^2/(2\mu\Delta R^2)](-1)^{i-j}P_{ij}, \quad (11a)$$

where

$$P_{ij} = \pi^2/3 \quad \text{for } i=j, \quad P_{ij} = 2/(i-j)^2 \quad \text{for } i \neq j, \quad (11b)$$

and  $\Delta R$  is the spacing of the grid. These equations follow, by differentiation, from the Lagrangian interpolation formula for equidistant arguments by extending the interpolated interval to  $\pm$  infinity while maintaining a fixed grid spacing. For a finite interpolation interval, they are valid, to a given accuracy, if the grid spacing  $\Delta R$  is taken sufficiently small so that the number of grid points becomes sufficiently large. The potential energy operator  $V(R)$  on the other hand, being a local operator, is diagonal as in all grid-based representations. Unlike a basis expansion method, this approach requires no computation of integrals over basis functions. The eigenvalue problem for the matrix of the Hamiltonian of Eq. (9) was solved by the EISPACK subroutines.<sup>108</sup> This method of solving Eq. (9) is applicable for any value of  $J$ .



The first grid point  $R_{\text{in}}$  and the last grid point  $R_{\text{out}}$  as well as the spacing  $\Delta R$  of the even-spaced grid points in between were obtained by monitoring the vibrational energy levels as functions of these three parameters. The end points  $R_{\text{in}}$  and  $R_{\text{out}}$  were chosen such that the wavefunction of the highest energy level had effectively converged to zero at these end points. The values  $R_{\text{in}}=1$  bohr and  $R_{\text{out}}=15$  bohrs were found to be adequate. As the number of grid points between them was increased from 100 to 1000 in increments of 100, all calculated energy levels exhibited no further change when the number of grid points exceeded 300. We used 500 points in all our calculations.

## B. Organization of spectral information

Following spectroscopic conventions,<sup>34</sup> we express the rotation-vibration energy levels in the form

$$E_{v,J} = V_{\text{eq}} + G_v + F_v(J), \quad (12)$$

where  $V_{\text{eq}}$  is the minimum value of the potential  $V(R)$  in Eq. (9) at the equilibrium distance  $R_{\text{eq}}$ , and  $v$  and  $J$  are the vibrational and rotational quantum numbers, respectively. By definition  $F_v(0)=0$  so that  $G_v$  is the pure vibrational spectrum.

Since the rotational energy in Eq. (9) is very small compared to the vibrational energy, the rotational term  $F_v(J)$  can be expanded as

$$F_v(J) = B_v[J(J+1)] - D_v[J(J+1)^2] + \dots \quad (13)$$

We determined theoretical  $B_v$  and  $D_v$  values by calculating the vibrational levels  $E_{v,J}$  for  $J$  values up to  $J=10$  and subsequent LMSQ fitting. As will be discussed in Sec. V, the first two terms of Eq. (13) always gave an excellent representation of  $F_v(J)$ . From first-order perturbation theory one also expects that

$$B_v = (\hbar^2/2\mu)\langle v|R^{-2}|v\rangle, \quad (14)$$

where  $|v\rangle$  denotes the wavefunction  $\psi_{v,J}$  of Eq. (10) for  $J=0$ .

According to Dunham,<sup>109</sup> the energy levels can be expanded as power series in terms of  $(v+\frac{1}{2})$  and  $[J(J+1)]$ , i.e.,

$$E_{v,J} = \sum_{km} Y_{km}(v+\frac{1}{2})^k [J(J+1)]^m. \quad (15)$$

Hence, the quantities  $G_v$ ,  $B_v$ , and  $D_v$  in Eqs. (12) and (13) are given by power series in  $(v+\frac{1}{2})$  as follows:

$$\begin{aligned} G_v &= \sum_k Y_{k0}(v+\frac{1}{2})^k \\ &= Y_{00} + \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \omega_e y_e(v+\frac{1}{2})^3 \\ &\quad + \dots, \end{aligned} \quad (16)$$

$$B_v = \sum_k Y_{k1}(v+\frac{1}{2})^k = B_e - \alpha_e(v+\frac{1}{2}) + \dots, \quad (17)$$

$$D_v = -\sum_k Y_{k2}(v+\frac{1}{2})^k = D_e + \beta_e(v+\frac{1}{2}) + \dots, \quad (18)$$

where the corresponding standard spectroscopic symbols have been inserted on the right hand side. The coefficients in

these expansions are known as Dunham coefficients or spectroscopic constants.<sup>34</sup> In first-order perturbation theory,  $B_e$  is related to the equilibrium distance by

$$B_e = (\hbar^2/2\mu)R_{\text{eq}}^{-2}. \quad (19)$$

Experiments can determine only the quantities

$$E_{v,J} - E_{00} = G(v) + F_v(J), \quad (20)$$

where  $G(v) = (G_v - G_0)$ , for which Eq. (16) yields the expansion

$$G(v) = G_v - G_0 = (Y_{00} - G_0) + \sum_{k=1} Y_{k0}(v+\frac{1}{2})^k. \quad (21)$$

When a good LMSQ fit of such an expansion to a given spectrum is valid, then the coefficients  $Y_{k0}$  for  $k \geq 1$  and the difference  $(Y_{00} - G_0)$  can be obtained by linear regression. According to Herzberg,<sup>110,111</sup> there moreover exists the relation

$$\begin{aligned} Y_{00} \approx Y_{00}^* &= \frac{1}{4}(Y_{20} + Y_{01}) + (-Y_{11}Y_{10}/12Y_{01}) \\ &\quad + (Y_{11}Y_{10}/12Y_{01})^2/Y_{01}, \end{aligned} \quad (22)$$

so that  $Y_{00}$  can be calculated from the higher  $Y$ -coefficients and the value of the zero-point energy  $G_0$  can then also be deduced. We shall discuss the applicability of this approach to the  $F_2$  spectrum in Sec. VI.

## IV. VIBRATIONAL SPECTRUM

### A. Comparison with the experimental spectrum

In 1976, Colbourn *et al.* experimentally determined the rovibrational spectrum of the  $F_2$  ground state by means of high-resolution electronic spectroscopy.<sup>95</sup> They stated that “errors in a few  $G(v)$  values may be as large as  $0.5 \text{ cm}^{-1}$  since the data came from many plates and absolute rather than relative errors determine our accuracy. We believe, however, that our method of treating the data has reduced most of the errors to less than  $0.2 \text{ cm}^{-1}$ .” On the other hand, we note that various authors<sup>112-114</sup> have given experimental values for  $G(1)$  that differ from that of Colbourn *et al.*<sup>95</sup> by deviations ranging between  $-1.88$  and  $+0.04 \text{ cm}^{-1}$ .

Our theoretically calculated vibrational spectra are compared with the experimentally observed spectrum in Table II. Except for the last five rows, each row in the table is labeled by the vibrational quantum number  $v$  in the first column and contains the data for  $G(v)$ . The second column lists the *experimental* value. Columns 3-7 contain the *theoretical* results calculated using the even-tempered representations given for the five alternative potential energy curves in the first five rows of Table I. The labels at the top of these columns identify the potentials and correspond to those used in Table I and explained in the text accompanying that table. Listed in these columns are the *deviations of the theoretically calculated levels from the spectroscopic values*, i.e.,

$$\Delta(v) = G(v; \text{theor.}) - G(v; \text{expt.}). \quad (23)$$

The row below  $v=22$  lists the MAD for each expansion.

The last four rows in Table II list the absolute values of the following spectroscopic quantities: zero-point energy

TABLE II. Comparison of experimental and *ab initio* calculated vibrational energy level differences  $G(v) = G_v - G_0$  in the electronic ground state of F<sub>2</sub>. Energies in cm<sup>-1</sup>.

$v$	Expt.	Theor. (deviation) <sup>a</sup>				
		EXTR1c	EXTR2c	EXTR3c	EXTR4c	EXTR5c
0	0.00	0.00	0.00	0.00	0.00	0.00
1	893.90	-1.79	-2.51	-1.21	-1.82	-2.24
2	1 764.15	-2.81	-4.09	-1.78	-2.96	-3.33
3	2 610.22	-3.19	-4.89	-1.85	-3.52	-3.43
4	3 431.53	-3.07	-5.06	-1.52	-3.63	-2.73
5	4 227.43	-2.57	-4.70	-0.87	-3.35	-1.36
6	4 997.19	-1.74	-3.89	0.04	-2.73	0.58
7	5 740.05	-0.68	-2.72	1.13	-1.84	2.97
8	6 455.17	0.55	-1.26	2.38	-0.71	5.73
9	7 141.63	1.90	0.43	3.73	0.62	8.77
10	7 798.48	3.27	2.26	5.10	2.07	11.97
11	8 424.67	4.57	4.13	6.43	3.58	15.23
12	9 019.11	5.66	5.89	7.57	5.00	18.37
13	9 580.63	6.33	7.34	8.34	6.17	21.20
14	10 108.02	6.31	8.18	8.45	6.79	23.39
15	10 599.62	5.54	8.38	7.88	6.83	24.91
16	11 053.90	3.65	7.56	6.24	5.91	25.38
17	11 468.96	0.36	5.43	3.25	3.74	24.52
18	11 842.62	-4.70	1.63	-1.46	-0.07	21.95
19	12 172.25	-11.89	-4.21	-8.30	-5.94	17.29
20	12 452.98	-19.98	-10.84	-16.09	-12.72	11.71
21	12 678.00	-26.70	-15.99	-22.67	-18.28	7.29
22	12 830.38	-21.04	-8.63	-17.32	-11.93	14.44
<b>MAD<sup>b</sup></b>		<b>6.29</b>	<b>5.46</b>	<b>6.07</b>	<b>5.01</b>	<b>12.22</b>
ZPE <sup>c</sup>	455.37	454.21	453.81	454.57	454.26	453.86
$D_0^d$	12 953.12	12 912.86	12 928.44	12 912.94	12 920.55	12 942.70
$D_e^e$	13 408.49 <sup>f</sup>	13 367.07	13 382.25	13 367.51	13 374.81	13 396.56
$R_e^g$	1.412 68 <sup>h</sup>	1.413 80	1.413 85	1.413 50	1.413 48	1.413 64

<sup>a</sup>Listed are the deviations: (theor. - expt.).<sup>b</sup>MAD=mean absolute deviation.<sup>c</sup>Zero-point energy.<sup>d</sup>Dissociation energy with respect to the lowest vibrational level. The experimental value is taken from Ref. 94.<sup>e</sup>Dissociation energy with respect to the lowest point on the potential energy curve.<sup>f</sup>Experimental uncertainty =  $\pm 8.07$  cm<sup>-1</sup> (see Ref. 94).<sup>g</sup>Equilibrium bond distance corresponding to the lowest point on the potential energy curve, in angstroms.<sup>h</sup>See Ref. 58.

(ZPE), dissociation energy  $D_0$  with respect to the lowest vibrational level, dissociation energy  $D_e$  with respect to the lowest point on the potential energy curve and equilibrium bond distance  $R_e$  corresponding to the lowest point on the potential energy curve.

For the four expansions EXTR1c–EXTR4c, the mean absolute deviations lie between 5.01 and 6.29 cm<sup>-1</sup> and the greatest deviations, viz., between 10 and 30 cm<sup>-1</sup>, occur only for the levels  $v=19$ –22. The best potential is EXTR4c. It may be noted that the difference of 1.28 cm<sup>-1</sup> between the MADs of the vibrational levels of EXTR1c and EXTR4c corresponds to a mean absolute deviation of about 0.03 mhartree  $\approx 7$  cm<sup>-1</sup> between the potentials themselves (see Table XI of the first paper of this series<sup>1</sup>).

As discussed in Sec. VI C of the first paper,<sup>1</sup> the potential EXTR5c was obtained using a somewhat flawed extrapolation of the triple-zeta  $\Delta E(4)$  values and was kept to examine the consequences. The mean absolute deviation of this flawed potential from the potential EXTR1c was

0.08 mhartree  $\approx 18$  cm<sup>-1</sup> (see Table XI of the first paper<sup>1</sup>). The corresponding MADs of the spectra of EXTR1c and EXTR5c differ by about 6 cm<sup>-1</sup>.

The range of the spectral deviations for the potentials EXTR1c–EXTR4c can be taken as indicative of the error bar inherent in the present *ab initio* calculations of the vibrational levels.

Infrared spectroscopy yields energy differences between neighboring levels, i.e.,  $[G_v - G_{v-1}]$ . They are displayed in Table III. The second column lists the experimental  $[G_v - G_{v-1}]$  values. The third and fourth columns give the theoretical results for the potential expansions EXTR3c and EXTR4c. Listed, as before, are the deviations of the theoretical values from the experimental values [see Eq. (23)]. The mean absolute deviation is seen to be about 2 cm<sup>-1</sup>. The fact that this value, though smaller by more than 50%, still is of the same order of magnitude as the value in Table II ( $\sim 5$ –6 cm<sup>-1</sup>) would seem to imply a random distribution of the theoretical errors over all levels.

TABLE III. Experimental and theoretical vibrational energy spacings  $G_v - G_{v-1}$ . Energies in  $\text{cm}^{-1}$ .

$v$	Expt.	Theor. (deviation) <sup>a</sup>	
		EXTR3c	EXTR4c
1	893.90	-1.21	-1.82
2	870.25	-0.57	-1.13
3	846.07	-0.06	-0.57
4	821.31	0.33	-0.10
5	795.90	0.64	0.28
6	769.76	0.91	0.62
7	742.86	1.10	0.89
8	715.12	1.24	1.13
9	686.46	1.35	1.33
10	656.85	1.38	1.45
11	626.19	1.33	1.51
12	594.44	1.14	1.43
13	561.52	0.77	1.17
14	527.39	0.11	0.62
15	491.60	-0.58	0.04
16	454.28	-1.64	-0.92
17	415.06	-2.99	-2.17
18	373.66	-4.71	-3.81
19	329.63	-6.84	-5.87
20	280.73	-7.79	-6.78
21	225.02	-6.58	-5.57
22	152.38	5.35	6.36
<b>MAD<sup>b</sup></b>		<b>2.21</b>	<b>2.07</b>

<sup>a</sup>Listed are the deviations (theor. - expt.).<sup>b</sup>Mean absolute deviation.

It should be noted that we have spent *no* special effort on refining the energy curve and its curvature *near the minimum* by calculating many energies near the equilibrium distance. Had we done so, it would undoubtedly have been possible to obtain a more accurate value for  $G(1)$ , as has been shown by others. The focus of our interest was, however, rather to reproduce the *entire* dissociation curve with as uniform an accuracy as possible since this had not been achieved before.

In as much as, in the first paper<sup>1</sup> of this series, we conservatively estimated possible errors in our correlation energy calculations to be about 50–60  $\text{cm}^{-1}$ , it is surprising to find a mean absolute deviation of only 5–10  $\text{cm}^{-1}$  between the calculated and the experimental spectra. Some light is shed on this matter, by the discussion above in Sec. II C, which showed that the average deviation from the best empirical potential is reduced by the even-tempered fitting of the *ab initio* data due to the random scattering of the latter. In addition, we believe that there exists some insensitivity of the vibrational eigenvalues with respect to small changes in a potential curve of this general shape.

## B. Relevance of the small *ab initio* contributions for the spectrum

How greatly is the spectrum really influenced by the small contributions that were determined in the preceding paper?<sup>2</sup> This question is answered by the data given in Table IV, where we used the potential expansion EXTR4c, which

yielded the best spectrum in Table II. The second column in Table IV lists the experimental spectrum; the subsequent columns list the spectra obtained from the following *ab initio* potentials.

- Third column: nonrelativistic; correlation only between valence electrons; but complete basis set limit; labeled “CBS.”
- Fourth column: CBS from third column plus core-generated electron correlations (i.e., core-core and core-valence correlations); labeled “CBS+CV.”
- Fifth column: CBS+CV from fourth column plus spin-orbit coupling; labeled “CBS+CV+SO.”
- Sixth column: CBS+CV+SO plus scalar relativistic contributions; labeled “CBS+CV+SO+SR” which is, in fact, the full EXTR4c potential.

In these columns, as in the previous tables, the deviations from experiment [see Eq. (23)] are listed. In order to calculate the various spectra via the discrete variable representation, we first determined the even-tempered Gaussian expansion for each case. As mentioned in Sec. II A, these expansions are listed in rows 6–8 of Table I.

Table IV shows that the omission of the “small corrections to the nonrelativistic valence-only-correlated complete-basis-set limit” deteriorates the mean absolute deviation of the spectrum by about 37  $\text{cm}^{-1}$ . Inclusion of the corrections is therefore essential. The largest improvements are due in about equal amounts to the core-generated correlations (about 19  $\text{cm}^{-1}$ ) and the spin-orbit coupling (about 18  $\text{cm}^{-1}$ ). The scalar relativistic correction yields only an improvement of less than 1  $\text{cm}^{-1}$ ; but it provides distinct improvements for the levels  $v=8-18$ .

## C. Comments on the highest vibrational levels

All theoretical potentials actually yield vibrational energy levels for  $v=0$  to  $v=23$ . Although Colbourn *et al.*<sup>95</sup> reported only experimental levels up to  $v=22$ , they admitted the possibility of the existence of higher levels beyond  $v=22$ , which their experiments were unable to detect due to the closeness to the dissociation limit. The optimal empirical potential  $W(R)$  of Sec. II C [which yields the three highest observed levels ( $v=20, 21, 22$ ) with a mean absolute deviation of 1  $\text{cm}^{-1}$ ] gives a value of 12 902.9  $\text{cm}^{-1}$  for  $G(23)$ .

The deviations of the individual  $G(v)$  values calculated with this empirical potential  $W(R)$  from the experimental values are graphically displayed in Fig. 2. The mean absolute deviation is 0.91  $\text{cm}^{-1}$ . Also shown in Fig. 2 are the deviations calculated with the RKR-derived potential (see Sec. II C) from the experimental values for  $v=1-21$ . The mean absolute deviation for these levels is 1.95  $\text{cm}^{-1}$ . The deviation for  $v=22$  is 18.4  $\text{cm}^{-1}$ .

There exists, however, the possibility that the highest vibrational levels are in fact the result of more complex interactions. In Sec. IV A of the preceding paper,<sup>2</sup> we have found that in the range of internuclear distances (about twice the equilibrium distance) where the highest levels have their turning points, the  $^1\Sigma_g$  ground state intersects a  $^3\Pi_u$  state, which lies lower at larger internuclear distances. In this re-

TABLE IV. Theoretical vibrational energy differences  $G(v)=G_v-G_0$  generated by a sequence of approximations to the full *ab initio* potential energy curve compared with the experimental differences. Energies in cm<sup>-1</sup>.

$v$	Expt.	Theor. (deviation) <sup>a</sup>			
		CBS <sup>b</sup>	CBS+CV <sup>c</sup>	CBS+CV +SO <sup>d</sup>	CBS+CV +SO+SR <sup>e</sup>
0	0.00	0.00	0.00	0.00	0.00
1	893.90	3.14	2.45	-1.35	-1.82
2	1 764.15	6.41	4.90	-2.02	-2.96
3	2 610.22	9.69	7.24	-2.13	-3.52
4	3 431.53	12.89	9.37	-1.79	-3.63
5	4 227.43	15.94	11.23	-1.07	-3.35
6	4 997.19	18.85	12.81	0.02	-2.73
7	5 740.05	21.60	14.11	1.29	-1.84
8	6 455.17	24.22	15.15	2.83	-0.71
9	7 141.63	26.77	15.99	4.58	0.62
10	7 798.48	29.29	16.66	6.44	2.07
11	8 424.67	31.86	17.26	8.35	3.58
12	9 019.11	34.55	17.82	10.18	5.00
13	9 580.63	37.40	18.41	11.76	6.17
14	10 108.02	40.45	19.04	12.78	6.79
15	10 599.62	44.06	20.05	13.23	6.83
16	11 053.90	48.34	21.57	12.73	5.91
17	11 468.96	53.68	23.94	10.99	3.74
18	11 842.62	60.57	27.63	7.62	-0.07
19	12 172.25	69.79	33.39	2.21	-5.94
20	12 452.98	84.18	43.99	-4.08	-12.72
21	12 678.00	108.31	63.94	-9.13	-18.28
22	12 830.38	156.70	107.61	-2.21	-11.93
<b>MAD<sup>f</sup></b>		<b>42.67</b>	<b>23.84</b>	<b>5.85</b>	<b>5.01</b>
ZPE <sup>g</sup>	455.37	456.80	456.52	454.50	454.26
$D_e^h$	13 408.49	13 727.80	13 656.53	13 385.84	13 374.81
$R_e^i$ (Å)	1.41268 <sup>j</sup>	1.41484	1.41309	1.41300	1.41348

<sup>a</sup>Listed are the deviations (theor. - expt.).<sup>b</sup>Nonrelativistic, valence-shell-only correlated, CBS limit for the potential EXTRA4.<sup>c</sup>As under footnote b plus correlations generated by core electrons.<sup>d</sup>As under footnote c plus spin-orbit coupling.<sup>e</sup>As under footnote d plus scalar-relativistic contributions=sixth column in Table II.<sup>f</sup>Mean absolute deviation.<sup>g</sup>Zero-point energy.<sup>h</sup>Dissociation energy relative to the minimum of the potential energy curve (see Table II).<sup>i</sup>Equilibrium distance corresponding to the minimum of the potential energy curve.<sup>j</sup>See Ref. 58.

gion, there exists therefore the possibility of a nonadiabatic coupling in conjunction with the spin-orbit coupling discussed in Sec. IV A of Ref. 2, which would then in fact determine the energies of the highest “vibrational” levels.

#### D. Equilibrium properties

The last four rows in Table II list the zero-point energy, the dissociation energy, and the equilibrium distance. Two dissociation energies are given: one  $D_0$  with respect to the lowest vibrational level  $G_0$ , and the other  $D_e$  with respect to the minimum of the dissociation curve.

The value of  $D_0$  is more directly related to experiment, although the complications of the long-range decay in F<sub>2</sub>, which were pointed out in Sec. IV A of the preceding paper,<sup>2</sup>

would seem to raise questions regarding the extrapolation to infinity in this molecule. Table II lists the experimental value obtained recently by Yang *et al.*,<sup>94</sup> viz.,  $12\,953.12 \pm 8.07$  cm<sup>-1</sup> which is expected to be more accurate than the previous experimental value of  $12\,920 \pm 50$  cm<sup>-1</sup> reported by Colbourn *et al.*,<sup>95</sup> as well as the earlier values of  $12\,824 \pm 80$  cm<sup>-1</sup> given by Berkowiz *et al.*<sup>115</sup> and  $12\,840$  cm<sup>-1</sup> listed by Stamper and Barrow.<sup>116</sup> Our theoretical values are obtained by assuming that the analytical expressions converge to the separate atom limit at infinity, i.e.,  $D_0 = V_{\text{eq}} + G_0 - V(\infty) = V_{\text{eq}} + G_0$ . The theoretical values differ at most by about 40 cm<sup>-1</sup> from the experimental value of Yang *et al.*<sup>94</sup>

We also list the value of  $D_e = V_{\text{eq}}$ , since this is an important intrinsic property of the analytical theoretical potentials. The difference  $(D_e - D_0) = G_0$ , the ZPE is also listed. The deduction of the experimental ZPE value will be discussed in Sec. VI B. Subtracting it from the experimental value of  $D_0$

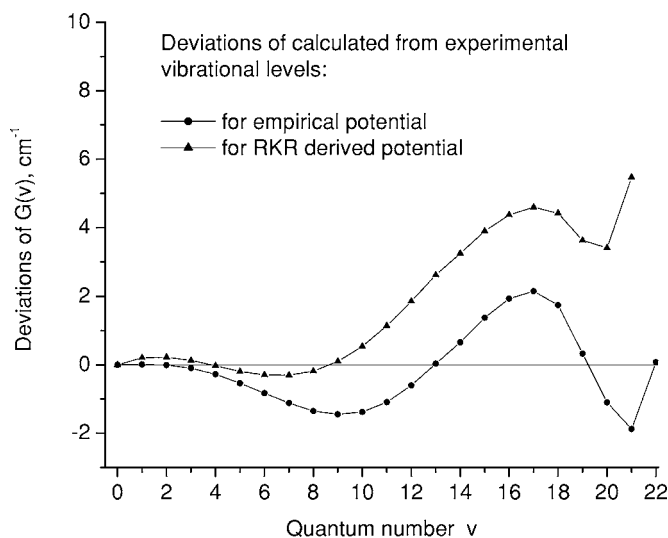


FIG. 2. Deviations of the  $G(v)$  values yielded by the RKR-derived potential and by the empirical potential for the vibrational levels of  $F_2$  from the corresponding experimental values. Plotted are calculated minus experimental values. Plotted are  $G(v; \text{fit}) - G(v; \text{expt.})$ .

gave the experimental value for  $D_e$ . The deviations between the theoretical and the experimental values of the zero-point energy are commensurate with those found for  $G(1)$ .

The theoretical equilibrium distances are the locations of the minima of the analytical dissociation curves. The determination of the “experimental equilibrium distances” will be discussed in Sec. VI B.

It may also be noted that, according to Table IV, the core-generated correlations shorten the equilibrium bond length by about  $0.0017 \text{ \AA}$ . This reduction is in agreement with the value of  $-0.0014 \text{ \AA}$  calculated for this effect by Ruden *et al.*<sup>58</sup>

## V. ROTATIONAL SPECTRUM

Colbourn *et al.*<sup>95</sup> deduced and reported values of  $B_v$  and  $D_v$  for all vibrational levels. We calculated the vibrational eigenvalues  $E_{vJ}$  for the angular momentum values  $J = 1, 2, \dots, 10$  and then examined the differences  $F_v(J) = E_{vJ} - E_{v0}$  for each  $v$  as functions of  $[J(J+1)]$ . Assuming the expression of Eq. (13) of Sec. III B, we determined the coefficients  $B_v$  and  $D_v$  by linear regression for the expansion

$$[F_v(J)/J(J+1)] = B_v - D_v[J(J+1)]. \quad (24)$$

In all cases, the mean absolute deviation between the left-hand side and the right-hand side of Eq. (13) ranged from  $10^{-6} \text{ cm}^{-1}$  for  $v=0$  to  $10^{-4} \text{ cm}^{-1}$  for  $v=22$ . We furthermore calculated alternative values of  $B_v$  by means of the expectation value formula of Eq. (14) in Sec. III B.

The results for the constants  $B_v$  are shown in Table V. Here we report only the values obtained with the potentials EXTR3c and EXTR4c since the other potentials EXTRnc of Table I yield extremely similar results. The second column of Table V lists the experimental values. The remaining four columns list the deviations of the theoretical values from the experimental values. Columns 3 and 4 contain the deviations for the potential EXTR3c, and columns 5 and 6 contain those for the potential EXTR4c. The values in columns 3 and 5 are

obtained from the fit of Eq. (23), whereas those in columns 4 and 6 were obtained from the expectation values by use of Eq. (14).

The mean absolute deviations are between  $0.0015$  and  $0.0019 \text{ cm}^{-1}$ . The average *relative* error is thus between  $0.2\%$  and  $0.5\%$  of the value of  $B_v$ , which varies between  $0.3365$  and  $0.8833 \text{ cm}^{-1}$ . Most of the lower levels have, however, considerably smaller deviations. The difference between the two ways of calculating  $B_v$  is on the average almost an order of magnitude smaller.

In this context, it should be mentioned that other experimenters have actually reported values of  $B_0$  (i.e., for the lowest vibrational level) that differ slightly from  $0.8833 \text{ cm}^{-1}$  (the value of Colbourn *et al.*<sup>95</sup>), namely,  $0.8829532$ ,<sup>112</sup>  $0.88331$ ,<sup>117</sup>  $0.8841$ ,<sup>118</sup>  $0.8847$ ,<sup>114</sup> and  $0.8828 \text{ cm}^{-1}$ .<sup>119</sup>

The results for the constants  $D_v$  are shown in Table VI. Most of them are about  $10^5$  times smaller than the  $B_v$  so that they are known with much less accuracy and the percentage disagreement is larger. We note that, whereas the theoretical values increase at a slow even pace in a steady monotonic fashion, the experimental values, while also increasing, exhibit erratic oscillations. Colbourn *et al.*<sup>95</sup> commented that the large random variations in the values of  $D_v$  are the result of errors in the rotational term values, whose experimental origin they explain. Making allowance for these problems, the agreement between *ab initio* values and experimental values is still good.

In the last column of Table VI, we also exhibit the mean absolute deviations for the *total* rotational fit, i.e., for  $\{F_v(J) - [B_v J(J+1) - D_v J^2(J+1)^2]\}$ . It demonstrates the adequacy of expanding  $F_v(J)$  as a quadratic in  $[J(J+1)]$ .

## VI. SPECTROSCOPIC CONSTANTS

### A. Expansion of vibrational energy levels in powers of $(v+1/2)$

The spectroscopic constants are based on the expression of the diatomic rotation-vibration levels as a power series in terms of  $(v+1/2)$  and  $[J(J+1)]$ , as has been formulated in Eqs. (15)–(18) of Sec. III B. It was first derived in 1932 by Dunham<sup>109</sup> on the basis of the WKB approximation. We have already commented on the expansion in terms of  $[J(J+1)]$  in the last paragraph of Sec. V. We shall now examine the expansion (16) of the vibrational levels, viz.,  $G_v = \sum_k Y_{k0}(v+1/2)^k$ . Understanding the sensitivity of this type of expansion with respect to the choice of the *range of the fitted levels* and to the *degree of the fitting polynomial* is prerequisite for a proper comparison of spectroscopic constants from different sources.

We first consider the theoretical energy levels. Table VII displays the Dunham expansions that were obtained by least squares fitting Eq. (16) to the levels resulting from our potential EXTR3c. Five *ranges of vibrational levels* were considered:  $v = \{0-2\}$ ,  $\{0-3\}$ ,  $\{0-4\}$ ,  $\{0-8\}$ , and  $\{0-16\}$ ; they are listed in separate sections of the table. Each row represents one expansion. The degree  $n$  of the *fitting polynomial* is listed in the first column. Columns 3–6 contain the four largest Dunham coefficients  $Y_{kn}$  resulting from the LMSQ fit.

TABLE V. Experimental and theoretical rotational constants  $B_v$  of the electronic ground state of F<sub>2</sub>. Units=cm<sup>-1</sup>.

$v$	Expt. <sup>a</sup> $B_v$	Theor. [EXTR3c] <sup>b</sup>		Theor. [EXTR4c] <sup>b</sup>	
		$B_v(\text{fit})^c$	$B_v(\text{calc})^d$	$B_v(\text{fit})^c$	$B_v(\text{calc})^d$
0	0.8833	-0.0017	-0.0013	-0.0017	-0.0013
1	0.8696	-0.0007	-0.0003	-0.0007	-0.0003
2	0.8560	-0.0001	0.0002	-0.0002	0.0002
3	0.8423	0.0001	0.0005	0.0001	0.0004
4	0.8284	0.0001	0.0005	0.0001	0.0004
5	0.8142	-0.0001	0.0003	-0.0001	0.0003
6	0.7996	-0.0004	0.0000	-0.0004	0.0000
7	0.7844	-0.0007	-0.0002	-0.0007	-0.0003
8	0.7685	-0.0009	-0.0005	-0.0009	-0.0005
9	0.7518	-0.0010	-0.0006	-0.0010	-0.0006
10	0.7343	-0.0012	-0.0007	-0.0012	-0.0007
11	0.7156	-0.0011	-0.0006	-0.0010	-0.0005
12	0.6958	-0.0009	-0.0004	-0.0008	-0.0002
13	0.6747	-0.0007	-0.0001	-0.0005	0.0001
14	0.6522	-0.0005	0.0002	-0.0003	0.0004
15	0.6282	-0.0005	0.0002	-0.0002	0.0005
16	0.6025	-0.0009	0.0000	-0.0005	0.0004
17	0.5750	-0.0019	-0.0010	-0.0015	-0.0005
18	0.5449	-0.0037	-0.0025	-0.0031	-0.0020
19	0.5094	-0.0042	-0.0028	-0.0036	-0.0022
20	0.4711	-0.0080	-0.0062	-0.0072	-0.0054
21	0.4185	-0.0064	-0.0039	-0.0056	-0.0031
22	0.3365	0.0084	0.0127	0.0095	0.0138
MAD <sup>e</sup>		0.0019	0.0016	0.0018	0.0015

<sup>a</sup>From Colbourn *et al.* (Ref. 95).<sup>b</sup>Entries list the differences:  $B_v(\text{theor.}) - B_v(\text{expt.})$ .<sup>c</sup>Calculated by linear regression, see Eq. (24).<sup>d</sup>Calculated as expectation value, see Eq. (14).<sup>e</sup>Mean absolute deviation.

The quantity  $Y_{00}^*$  in the second column is the approximation to  $Y_{00}$  that is obtained from the higher  $Y$  coefficients by using the Herzberg equation (22). The coefficients for  $k \geq 4$  are not listed since they are an order of magnitude smaller. They are, however, included in the mean absolute deviation of the fit, which is listed in the last column. A figure “0” without decimals in that column indicates that this is an exact rather than a LMSQ fit, the number of coefficients being equal to the number of levels fitted.

The data for the ranges {0–8} and {0–16} clearly show that all coefficients strictly and rapidly converge as the degree of the polynomial increases and, furthermore, that *the convergence limits are the same for these two ranges*. Moreover, these convergence limits are practically identical with the values of the exact expansions for the ranges {0–4} and {0–3}. The coefficients of the third degree polynomial for the range {0–4} are also close. For the ranges {0–8} and {0–16}, convergence has, however, *not* been reached by the third degree polynomials. The second-degree polynomial does not yield the converged values for any range, especially not for  $Y_{00}$ . Finally, we note that the approximation  $Y_{00}^*$  agrees with  $Y_{00}$  within 0.01 cm<sup>-1</sup> (i.e., ~5% of its value of ~0.2 cm<sup>-1</sup>) whenever convergence is reached. The converged polynomial representation is thus *unique* and it is obvious that, for the same accuracy, a small range of levels naturally requires

fewer powers of the expansion than a large range. Therefore, the lower Dunham coefficients  $Y_{10}$ ,  $Y_{20}$ , and  $Y_{30}$  are manifestly determined by the energy levels  $v = \{0-4\}$ .

Now let us consider “quantum mechanically refined experimental levels,” which result from solving the Schrödinger equation for an appropriate *analytical* potential energy expression that yields levels within the experimental uncertainty of the experimental measurements. In the present case, we have two analytical potentials that meet this requirement for the lower levels, which determine the lower Dunham coefficients. They were discussed in Sec. II C: One is the even-tempered fit to the RKR potential, listed in the second to last row of Table I; the other is our best empirical even-tempered potential listed in the last row of Table I. The deviations of the levels calculated using both potentials from the experimental levels had been displayed in Fig. 2. The plots in Fig. 3, exhibiting these deviations for the levels  $v = 1-4$ , show that both potentials yield levels 1–4 within the error bar of 0.2 cm<sup>-1</sup> estimated by the experimentalists.<sup>95</sup>

Consider first the levels resulting from our best empirical potential. The Dunham coefficients obtained by least mean squares fitting these levels are listed in Table VIII, which is organized in exactly the same way as Table VII. The coefficients in this table manifestly exhibit the same excellent convergence behavior as those in Table VII resulting in unique

TABLE VI. Rotational constants  $D_v$  and total fits of the rotational terms  $F_v(J)$  for the electronic ground state of  $F_2$ . Energies in  $10^{-6} \text{ cm}^{-1}$ .

$v$	Expt. <sup>a</sup> $D_v$	Theor. <sup>b</sup>		Total rot. deviation <sup>c</sup>
		$D_v$ (fit) <sup>c</sup>	$D_v$ (fit) <sup>d</sup>	
0	3.3	3.4	3.4	1.7
1	3.1	3.4	3.4	0.7
2	2.7	3.5	3.5	0.7
3	4.4	3.6	3.6	0.4
4	3.6	3.7	3.7	0.8
5	2.2	3.9	3.9	1.5
6	4.6	4.0	4.0	0.6
7	4.5	4.2	4.2	1.5
8	5.2	4.4	4.4	1.1
9	5.4	4.6	4.6	1.5
10	6.5	4.9	4.9	1.9
11	6.7	5.2	5.2	3.0
12	3.7	5.6	5.6	3.3
13	9.2	6.0	6.0	3.9
14	8.5	6.6	6.6	5.1
15	5.5	7.3	7.3	7.0
16	8.6	8.2	8.2	9.6
17	7.0	9.5	9.4	13.8
18	9.8	11.2	11.1	21.1
19	15.0	13.6	13.6	34.7
20	19.6	17.6	17.5	64.7
21	32.7	24.7	24.5	148
22	86.4	41.8	41.4	558

<sup>a</sup>From Colbourn *et al.* (Ref. 95).<sup>b</sup>Calculated by linear regression, see Eq. (24).<sup>c</sup>Energy levels calculated from potential EXTR3c.<sup>d</sup>Energy levels calculated from potential EXTR4c.<sup>e</sup>MAD of total rotational fit  $\{F_v(J) - [B_v J(J+1) - D_v J^2(J+1)^2]\}$  for fixed value of  $v$ .

converged values. The same excellent convergent behavior is furthermore also found when we consider the analogous results for the RKR-derived potential. The converged coefficients of the analytic RKR-derived potential compare with those of the best empirical potential in Table VIII as follows:

	$Y_{00}$	$Y_{10}$	$Y_{20}$	$Y_{30}$
RKR	-0.55	917.55	-11.62	-0.06
Empirical	-0.31	917.07	-11.44	-0.09

According to the preceding discussion, the differences between *these*  $Y$ -values from the two potentials is a consequence of the differences in the *lowest* levels calculated from the two potentials. Since we saw in Fig. 3 that the latter differences stay within the experimental uncertainty, it follows that the differences in these  $Y$ -values reflect the experimental uncertainties. Thus, the experimental spectrum does *not* determine the harmonic frequency  $\omega_e = Y_{10}$ , for instance, more accurately than by  $0.5 \text{ cm}^{-1}$ .

Furthermore, since, according to Fig. 3, the lowest four levels of our best empirical potential approximate the experimental levels markedly more closely than those of the RKR-derived potential, one would infer the following most reasonable estimates from the experimental data (in  $\text{cm}^{-1}$ ):

$$Y_{00} = -0.31 \pm 0.2, \quad Y_{10} = 917.07 \pm 0.5, \quad (25a)$$

$$Y_{20} = -11.44 \pm 0.2, \quad Y_{30} = -0.09 \pm 0.03. \quad (25b)$$

Thus, we draw the following conclusions for *accurate solutions of the vibrational Schrödinger equation*.

- The least mean squares fits of the Dunham coefficients to the energy levels converge with respect to the expansion range and the polynomial degree as illustrated.
- Only the converged constants are unique characteristics of the spectrum. In the present case, the polynomials for  $n=6$  in the range  $v=\{0-8\}$  appear to be appropriate choices and they have been indicated by boldface font.
- One would obtain arbitrary deviations from the converged values if one were to use a *low-order* (e.g., third order) polynomial to fit the range  $\{0-8\}$ .
- The converged values are sensitive to the accuracy with which the levels have been determined as well as to slight changes in the potential.

## B. Expansion of vibrational transition energies in powers of $(v+1/2)$

Since only the transition energies, i.e., the level differences  $G(v) = G_v - G_0$ , can be measured experimentally, one is led to ask whether the Dunham expansion can be used directly with the differences, i.e., without the “detour” over an empirical potential and the Schrödinger equation discussed in the preceding section. A particular question is whether the zero-point energy, i.e., the lowest level  $G_0$ , can be deduced.

Consider first the spectra that have resulted from solving the Schrödinger equation, whose Dunham coefficients were listed in Tables VII and VIII. Imagine that only the differences  $G(v) = G_v - G_0$  are available to us, and that we perform the LMSQ fitting on these values, including  $G(0)=0$ . Doing so will yield exactly the same numerical values as before in all columns of Tables VII and VIII (including  $Y_{00}^*$ !) with the sole exception that, in the third column, the constant term becomes now  $Z_0 = (Y_{00} - G_0)$  rather than  $Y_{00}$ . In the case of any one of the *converged* polynomial expansions, one can therefore deduce, to a good approximation, the lowest level  $G_0$  by substituting  $Y_{00}^*$  for  $Y_{00}$  in  $Z_0$ , whence  $G_0 = (Y_{00}^* - Z_0)$ . The errors in  $G_0$  will be the differences  $(Y_{00} - Y_{00}^*) = 0.013$  and  $0.007 \text{ cm}^{-1}$ , in Tables VII and VIII, respectively.

Now, let us consider LMSQ fitting to the raw experimental data in the same manner. Table IX exhibits the expansion coefficients that we obtained by fitting Dunham polynomials directly to the experimental data of Colbourn *et al.*,<sup>95</sup> which had been listed in the second column of Table II. Table IX is organized exactly as Table VIII, except that the third column contains now  $Z_0 = (Y_{00} - G_0)$  rather than  $Y_{00}$ , as was discussed in the preceding paragraph.

While the convergence of the coefficients in Table IX exhibits the same general pattern as that in Table VIII, it manifestly is not as good. There is a marked random scatter in the data so that, e.g., the first decimal in  $Y_{10}$  is uncertain.

TABLE VII. Convergence of various expansions of the theoretical (this work, using the potential energy curve EXTR3c) vibrational levels  $G_v$  in terms of powers of  $(v+1/2)$ . Energy unit= $\text{cm}^{-1}$ .

$n$	$Y_{00}^*$	$Y_{00}$	$Y_{10}$	$Y_{20}$	$Y_{30}$	MAD
			$v=\{0-2\}$			
2	-0.3095	-0.4054	915.703	-11.507	...	0
			$v=\{0-3\}$			
2	-0.3488	-0.6274	916.163	-11.671	...	0.0658
3	-0.1887	-0.1998	915.073	-11.013	-0.1096	0
			$v=\{0-4\}$			
2	-0.3888	-0.9919	916.774	-11.841	...	0.1628
3	-0.1845	-0.1895	915.045	-10.996	-0.1126	0.0016
4	-0.1966	-0.2096	915.105	-11.045	-0.0977	0
			$v=\{0-8\}$			
2	-0.5568	-4.8372	920.932	-12.578	...	1.4605
3	-0.1535	-0.0160	914.725	-10.867	-0.1268	0.0466
4	-0.2020	-0.2229	915.139	-11.068	-0.0924	0.0019
5	-0.1948	-0.2074	915.098	-11.038	-0.1009	0.0001
<b>6</b>	<b>-0.1958</b>	<b>-0.2088</b>	<b>915.102</b>	<b>-11.042</b>	<b>-0.0992</b>	<b>0.0001</b>
7	-0.1956	-0.2086	915.102	-11.041	-0.0996	0.0000
8	-0.1957	-0.2087	915.102	-11.042	-0.0993	0
			$v=\{0-16\}$			
2	-0.9516	-39.4633	941.093	-14.480	...	13.7584
3	0.0329	3.6127	910.990	-10.062	-0.1733	1.1833
4	-0.2763	-0.7844	916.004	-11.378	-0.0532	0.1536
5	-0.1689	-0.1076	914.893	-10.931	-0.1227	0.0210
6	-0.2046	-0.2292	915.155	-11.078	-0.0889	0.0030
7	-0.1927	-0.2039	915.088	-11.029	-0.1040	0.0005
8	-0.1967	-0.2098	915.106	-11.045	-0.0976	0.0001
9	-0.1953	-0.2083	915.101	-11.040	-0.1002	0.0000

This affects, in particular, the small quantity  $Y_{00}^*$ . Consider, for instance, the range  $\{0-8\}$ : Whereas in Table VIII the value of  $Y_{00}^*$  varied by at most  $0.001 \text{ cm}^{-1}$  between the polynomials  $n=6,7,8$ , this variation now goes from  $0.01$  to  $0.1 \text{ cm}^{-1}$  in Table IX. This scattering interferes with

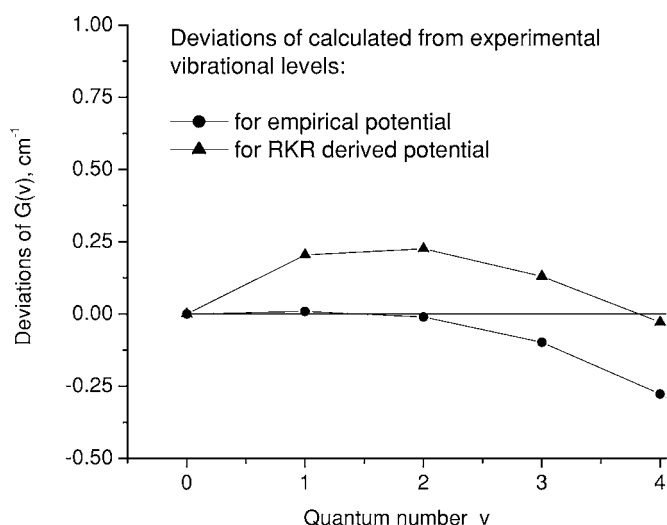


FIG. 3. Deviations of the  $G(v)$  values yielded by the RKR-derived potential and by the empirical potential for the lower vibrational levels of F<sub>2</sub> from the corresponding experimental values. Plotted are calculated minus experimental values. Plotted are  $G(v;\text{fit})-G(v;\text{expt.})$ .

identifying converged values in Table IX. A reasonable choice appears to be given by the coefficients for  $n=6$  and  $v=\{0-8\}$  and they happen to be close to the corresponding coefficients in Table VIII, including  $Y_{00}^*$ .

These results imply that fitting the differences  $G(v) = G_v - G_0$  also yields Dunham coefficients that converge very well (including  $Y_{00}^*$ ) provided these differences are given with the high accuracy that was available for our solutions of the Schrödinger equation with an analytical potential. This is not so, however, for experimental levels with an inaccuracy of  $0.2-0.5 \text{ cm}^{-1}$ , which is that stated by Colbourn *et al.*<sup>95</sup>

As has been exemplified in the preceding section, this convergence problem can be bypassed if one can find an analytical potential that recovers the experimental levels via the Schrödinger equation to experimental accuracy. For such a “quantum mechanically refined” experimental level, the LMSQ fitting will then yield converged Dunham coefficients and also, of course, directly the zero-point energy  $G_0$ .

A comparison of the data in Table IX with the Dunham coefficients that Colbourn *et al.*<sup>95</sup> have deduced from fitting to the level range  $\{0-8\}$ , viz.,

$$Y_{10} = 916.64, \quad Y_{20} = -11.236, \quad Y_{30} = -0.113,$$

suggests that these values were obtained by fitting a *third* degree polynomial to the level range chosen by these authors, i.e.,  $\{0-8\}$ . This is, however, an inappropriate poly-



TABLE VIII. Convergence of various expansions of the vibrational levels  $G_v$  in terms of powers of  $(v+1/2)$  based on nearly exact empirical potential. Energy unit= $\text{cm}^{-1}$ .

$n$	$Y_{00}^*$	$Y_{00}$	$Y_{10}$	$Y_{20}$	$Y_{30}$	MAD
			$v=\{0-2\}$			
2	-0.3993	-0.4782	917.587	-11.839	...	0
			$v=\{0-3\}$			
2	-0.4334	-0.6708	917.986	-11.982	...	0.0571
3	-0.2945	-0.2998	917.040	-11.411	-0.0951	0
			$v=\{0-4\}$			
2	-0.4681	-0.9874	918.516	-12.129	...	0.1414
3	-0.2907	-0.2906	917.015	-11.395	-0.0978	0.0015
4	-0.3016	-0.3086	917.069	-11.440	-0.0844	0
			$v=\{0-8\}$			
2	-0.6146	-4.3416	922.142	-12.772	...	1.2754
3	-0.2624	-0.1324	916.724	-11.278	-0.1107	0.0426
4	-0.3068	-0.3214	917.102	-11.461	-0.0793	0.0019
5	-0.2998	-0.3065	917.062	-11.433	-0.0875	0.0001
<b>6</b>	<b>-0.3008</b>	<b>-0.3079</b>	<b>917.067</b>	<b>-11.437</b>	<b>-0.0857</b>	<b>0.0000</b>
7	-0.3007	-0.3078	917.066	-11.436	-0.0859	0.0000
8	-0.3008	-0.3078	917.067	-11.437	-0.0858	0
			$v=\{0-16\}$			
2	-0.9645	-35.0775	940.017	-14.456	...	12.2592
3	-0.0869	3.2992	913.198	-10.520	-0.1544	1.1281
4	-0.3813	-0.8876	917.972	-11.773	-0.0400	0.1563
5	-0.2720	-0.1990	916.841	-11.318	-0.1107	0.0229
6	-0.3109	-0.3315	917.127	-11.478	-0.0739	0.0035
7	-0.2970	-0.3018	917.049	-11.421	-0.0917	0.0006
8	-0.3020	-0.3093	917.072	-11.442	-0.0835	0.0001
9	-0.3002	-0.3073	917.065	-11.434	-0.0871	0.0000

mial choice for this range, as has been discussed above, and these values, which are also quoted in Ref. 34, should therefore be replaced by those given above in Eq. (25).

### C. Spectroscopic constants

The larger coefficients in the Dunham expansion are known as spectroscopic constants and have simple physical meanings regarding vibration and rotation. They serve as useful condensations of molecular characteristics, as is evidenced by the renown of the collection by Huber and Herzberg.<sup>34</sup> They also provide a standardized vehicle for comparing results from various sources, experimental as well as theoretical. It has also been demonstrated<sup>120</sup> that certain quantitative correlations exist between the spectroscopic constants of different but related diatomic molecules. They embody of course less information than the full spectrum. But very often neither an accurate full potential energy curve nor a full spectrum is available.

Table X compares the spectroscopic constants relating to the vibrational spectrum of  $F_2$  that are obtained from various sources. Columns 2–6 list the Dunham coefficients. Columns 7, 8, and 9 list the zero-point energies  $G_0$ , the dissociation energy relative to the lowest vibrational level  $D_0$ , and the dissociation energy relative to the minimum of the potential energy curve  $D_e$ , respectively.

The values quoted in the first row for the electronic spec-

troscopic experiments of Colbourn *et al.*<sup>95</sup> are those we have obtained in Eq. (25) of the preceding section. There, we also gave the uncertainties in these values that follow from the experimental uncertainties and we explained the reasons for preferring these values to those given by Colbourn *et al.*<sup>95</sup> and subsequently quoted by Huber and Herzberg.<sup>34</sup> They turn out to be quite close to the results of the experimental work of Martinez *et al.*,<sup>112</sup> listed in the third row of Table X. These authors determined the lowest levels extremely accurately and determined the Dunham constants essentially from them.

The experimental value of the zero-point energy  $G_0$  in the first row came directly from the levels of the analytic fit whereas, in the second row, it was deduced from the values of  $Z_0=(Y_{00}-G_0)$  and  $Y_{00}^*$  of the selected polynomial in Table IX, as discussed in the preceding section. The value of  $D_e$  in this row was obtained by adding  $G_0$  to the experimental value of  $D_0$  (see Ref. 94).

The next two rows list the constants obtained from two of our theoretical potential energy curves, viz., EXTR3c and EXTR4c. Using any of our other variants would change the constants very little. For instance,  $\omega_e$  would change by about a half of a wavenumber and the dissociation energies  $D_0$  fall in the range from 12 910 to 12 930  $\text{cm}^{-1}$ , bracketing the experimental value  $12\,920 \pm 50 \text{ cm}^{-1}$  of Colbourn *et al.*<sup>95</sup> within the experimental uncertainty. When compared to the more recent and presumably more accurate experimental

TABLE IX. Convergence of various expansions of the experimental vibrational transitions  $G(v)=G_v-G_0$  in terms of powers of  $(v+1/2)$ . Energy unit= $\text{cm}^{-1}$ .

$n$	$Y_{00}^*$	$Z_0=Y_{00}-G_0$	$Y_{10}$	$Y_{20}$	$Y_{30}$	MAD
			$v=\{0-2\}$			
2	-0.3819	-455.8188	917.550	-11.825	...	0
			$v=\{0-3\}$			
2	-0.4135	-455.9976	917.921	-11.958	...	0.0530
3	-0.2845	-455.6531	917.042	-11.428	-0.0883	0
			$v=\{0-4\}$			
2	-0.4464	-456.2979	918.424	-12.097	...	0.1341
3	-0.2786	-455.6388	917.004	-11.403	-0.0925	0.0023
4	-0.2955	-455.6668	917.088	-11.472	-0.0717	0
			$v=\{0-8\}$			
2	-0.5945	-459.7123	922.104	-12.748	...	1.3130
3	-0.2328	-455.3888	916.538	-11.213	-0.1137	0.0633
4	-0.2988	-455.6701	917.101	-11.486	-0.0669	0.0016
5	-0.3028	-455.6786	917.124	-11.502	-0.0623	0.0012
<b>6</b>	<b>-0.2982</b>	<b>-455.6724</b>	<b>917.104</b>	<b>-11.483</b>	<b>-0.0700</b>	<b>0.0011</b>
7	-0.2529	-455.6285	916.946	-11.299	-0.1692	0.0005
8	-0.3604	-455.7113	917.270	-11.735	0.1172	0
			$v=\{0-16\}$			
2	-0.9568	-491.4113	940.583	-14.493	...	12.5421
3	-0.0599	-452.1616	913.154	-10.468	-0.1579	0.9850
4	-0.3195	-455.8538	917.364	-11.573	-0.0570	0.0735
5	-0.2705	-455.5452	916.858	-11.369	-0.0887	0.0390
6	-0.3312	-455.7520	917.303	-11.618	-0.0312	0.0159
7	-0.2790	-455.6404	917.010	-11.405	-0.0981	0.0083
8	-0.2867	-455.6520	917.045	-11.436	-0.0854	0.0078
9	-0.3886	-455.7688	917.438	-11.850	0.1176	0.0075

value of Yang *et al.*<sup>94</sup> of  $12\,953 \pm 8 \text{ cm}^{-1}$  (see the third row from the bottom of Table II), the theoretical values for  $D_0$  deviate by about 40 and  $30 \text{ cm}^{-1}$  for the EXTR3c and EXTR4c potential curves, respectively.

The Dunham coefficients of our theoretical work based on EXTR3c potential deviate from the experimental data of  $(Y_{00}-G_0)$ ,  $Y_{10}$ ,  $Y_{20}$ ,  $Y_{30}$ , and  $Y_{40}$  by 0.9, -2.0, 0.4, -0.03, and  $4.0 \times 10^{-4} \text{ cm}^{-1}$ , respectively, which are commensurate with the deviations in the spectrum discussed in Sec. IV. In this context, it should be kept in mind that the present theoretical effort is aimed at the global surface and that no special effort was made to refine the description of the potential energy surface near the equilibrium geometry by calculating a denser array of points in that neighborhood.

The third section of Table X contains data based on other *ab initio* work.<sup>56,58,71-75</sup> By far the most accurate of them is that by Ruden *et al.*,<sup>58</sup> which is based on a high-level CC5/R12 theory including core correlation and relativity corrections. These authors obtained a value of  $Y_{10}=\omega_e$  that is about  $1.8 \text{ cm}^{-1}$  larger than the converged “experimental” value of  $917.1 \text{ cm}^{-1}$ . The remaining theoretical values correspond to lower levels of theory and yield  $\omega_e$  values deviating between -17 and  $+39 \text{ cm}^{-1}$  from the experimental result. The only *ab initio* calculation reporting the three Dunham coefficients  $Y_{10}$ ,  $Y_{20}$ , and  $Y_{30}$  is the Møller-Plesset Epstein-Nesbet (MP-EN) calculation of Angeli *et al.*<sup>56</sup> It should be noted that most of the “other theoretical results” listed in Table X do

not consider core-electron correlations and relativity effects (including spin-orbit coupling). These omissions can considerably alter the values of the spectroscopic constants. For instance, according to Table IV of the preceding paper,<sup>2</sup> these corrections lower the dissociation energy  $D_e$  by about  $343 \text{ cm}^{-1}$ , and the Dunham expansion of the data in the third column in Table IV of the present paper leads to a reduction of the harmonic frequency by  $5 \text{ cm}^{-1}$  when the (CV+SO+SR) corrections are added to CBS result.

The spectroscopic constants related to the rotational spectrum of F<sub>2</sub> obtained from various sources are compared in Table XI. Experimental values are available from high-resolution electronic spectroscopy,<sup>95</sup> from high-resolution stimulated Raman spectroscopy,<sup>112</sup> and from low-resolution spontaneous Raman spectroscopy.<sup>117</sup> They are listed in the first three rows of Table XI. A “mixed” approach, quoted in the fourth row, has recently been advanced by Pawłowski *et al.*<sup>121</sup> namely, to combine the experimental value of  $B_0$  with the theoretical value of  $\alpha_e$  to calculate  $B_e$ .

Experimentally, the rotational constants  $B_e$  and  $\alpha_e$  are obtained by expanding  $B_v$  according to Eq. (17) of Sec. III B. The  $B_v$  are experimentally obtained by the expansion of Eq. (13), as discussed in Sec. V. The internuclear distance, in turn, is obtained from  $B_e$  according to Eq. (19).

Theoretically,  $B_v$  can also be calculated as an expectation value according to Eq. (14). The values from the present

TABLE X. Comparison of vibrational spectroscopic constants of F<sub>2</sub>. All energies in cm<sup>-1</sup>.

Source	$Y_{00}-G_0$	$Y_{10}=\omega_e$	$Y_{20}=-\omega_e x_e$	$Y_{30}=\omega_e y_e$	$Y_{40}=\omega_e z_e$	$G_0^a$	$D_0^a$	$D_e^a$
Experimental values								
El. sp. best PES <sup>b</sup>	-455.66	917.067	-11.4369	-0.08573	$-1.0834 \times 10^{-3}$	455.36		
El. sp. direct fit <sup>c</sup>	-455.67	917.104	-11.4835	-0.06997	$-1.6223 \times 10^{-3}$	455.37	12 953	13 408
Stim. Raman (Ref. 112) <sup>d</sup>		916.929	-11.3221	-0.10572				
Present theoretical values								
CEEIS(3c) <sup>e</sup>	-454.78	915.102	-11.0420	-0.09920	$-1.2031 \times 10^{-3}$	454.57	12 913	13 368
CEEIS(4c) <sup>f</sup>	-454.45	914.444	-11.0206	-0.09812	$-1.1021 \times 10^{-3}$	454.26	12 921	13 375
Other theoretical values								
CC-5/R12 (Ref. 58)		918.9						
CCSD(T) (Ref. 74) <sup>g</sup>		955.5						13 358
ic-MRCI+Q (Ref. 74) <sup>g</sup>		916.9						12 851
MkCCSD (Ref. 75) <sup>g,h</sup>		915.0						13 466
ic-MRCI (Ref. 71) <sup>g,h</sup>		899.7	-12.48					12 019
CASPT3 (Ref. 71) <sup>g,h</sup>		920.0	-12.62					11 856
(mv)td-2 (Ref. 72) <sup>g,h</sup>		915.2	-10.4					12 824
(mv)td-2' (Ref. 72) <sup>g,h</sup>		916.0	-10.1					12 824
MP-EN (Ref. 56) <sup>g,h</sup>		924.4	-10.45	-0.143				14 301
4R RMR CCSD(T) (Ref. 73) <sup>g,h</sup>		911.2	-10.98					

<sup>a</sup> $G_0$ =zero-point energy,  $D_0$ =dissociation energy from  $G_0$ , and  $D_e$ =dissociation energy from potential curve minimum (see text).

<sup>b</sup>From best analytical empirical potential for electronic spectrum. Dunham fit: sixth degree polynomial for the level range {0–8}.

<sup>c</sup>Direct Dunham fit to the high-resolution electronic spectrum: sixth degree polynomial for the level range {0–8}.

<sup>d</sup>From stimulated Raman emission spectrum.

<sup>e</sup>This work, using the potential energy curve EXTR3c. Dunham fit: sixth degree polynomial for the range {0–8}.

<sup>f</sup>This work, using the potential energy curve EXTR4c. Dunham fit: sixth degree polynomial for the range {0–8}.

<sup>g</sup>Relativistic corrections not included.

<sup>h</sup>1s-electrons are not correlated.

TABLE XI. Comparison of rotational spectroscopic constants of F<sub>2</sub>. Energies in cm<sup>-1</sup>; distances in Å.

Source	$B_e$	$\alpha_e$	$R_e(B)^a$	$R_e(V)^b$
Experimental values				
Electronic spectroscopy (Refs. 34 and 95) <sup>c</sup>	0.890 19	0.013 8	1.411 93	
Rotational Raman spectroscopy (Ref. 117)	0.889	0.011	1.412 9	
Stimulated Raman emission (Ref. 112)	0.889 294	0.012 595 2	1.412 642	
$B_e$ from experimental $B_0$ and <i>ab initio</i> $\alpha_e$ (Ref. 121)	0.889 24	0.012 57	1.412 68	
Theoretical values				
This work, potential EXTR3c <sup>c,d</sup>	0.887 84	0.012 4	1.413 8	1.4135
This work, potential EXTR3c <sup>c,e</sup>	0.888 20	0.012 3	1.413 5	1.4135
CC-5/R12+relativity, all el. corr. (Ref. 58)				1.4122
CC-5/R12+relativity, all el. corr. (Ref. 59)				1.4118
CCSD(T), all el. corr./cc-pCV6Z (Ref. 74) <sup>f</sup>				1.4087
ic-MRCI+Q, all el. corr./cc-pCV5Z (Ref. 74) <sup>f</sup>				1.4105
FDD-MR(C)/NEVPT3, cc-pVQZ (Ref. 55) <sup>f,g</sup>				1.4129
MRCI, cc-pV5Z (Ref. 71) <sup>f,g</sup>	0.888	0.013 6	1.413 7	
CASPT3, cc-pV5Z (Ref. 71) <sup>f,g</sup>	0.894	0.013 3	1.409 1	
(mv)td-2, 5s4p3d2f1g basis (Ref. 72) <sup>f,g</sup>	0.890 4	0.013 5	1.411 8	1.413
(mv)td-2', 5s4p3d2f1g basis (Ref. 72) <sup>f,g</sup>	0.891 2	0.013 4	1.411 1	1.413
MP-EN, 7s7p4d3f ANO basis (Ref. 56) <sup>f,g</sup>				1.411
4R RMR CCSD(T), cc-pVQZ (Ref. 73) <sup>f,g</sup>	0.884	0.012 6	1.417	1.416
CBS MkCCSD (Ref. 75) <sup>f,g</sup>				1.4134

<sup>a</sup>Calculated from  $B_e$ .

<sup>b</sup>Location of minimum on the potential energy curve.

<sup>c</sup> $B_e$  calculated by fit to  $B_v$  using  $(v+1/2)$  to the second order and range  $v=\{0-2\}$ .

<sup>d</sup> $B_v$  is calculated by linear regression [ $J=\{1-10\}$ ], see Eq. (24)].

<sup>e</sup> $B_v$  is calculated as the expectation value of the wavefunction [Eq. (14)].

<sup>f</sup>Nonrelativistic calculation.

<sup>g</sup>1s-electrons are not correlated.

theoretical work, labeled CEEIS, quoted in the fifth and sixth rows of Table X differ in this respect and show that the fourth decimal in  $B_e$  is affected by this methodological alternative. Theoretically, the equilibrium distance can also be calculated as the position of the minimum on the potential energy curve and the CEEIS results show that this difference in definition affects the fourth decimal of the distance in angstroms.

The close agreement between the values obtained for these constants by the various experimental and theoretical approaches shows that all of them are largely determined by the rotational structure of the lowest three vibrational energy levels.

## VII. SUMMARY

In the present series of three papers, the full theoretical route from the *ab initio* quantum-chemical calculation of the potential energy surface to the entire vibration-rotation spectrum has been traversed, without any empirical adjustments, for the 18 electrons in the ground state of the fluorine molecule. Electron correlations involving valence electrons were calculated using the correlation energy extrapolation by intrinsic scaling<sup>122–126</sup> (CEEIS) method and the complete-basis-set limit of these nonrelativistic energies was determined. Electron correlations involving core electrons, spin-orbit coupling, as well as scalar relativistic corrections were accounted for. Spin-spin coupling was deemed negligible since unpaired spins emerge only upon approaching separation of the atoms, at which point the large internuclear distance suppresses these interactions. Also omitted were the diagonal non-Born-Oppenheimer corrections since previous work had shown them to be negligible, as discussed in the concluding section of the preceding paper.<sup>2</sup> A novel analytical form, the even-tempered expansion, was introduced for the potential energy curve and found to provide a close fit to the *ab initio* energies over the entire distance range. With it the vibration and rotation spectrum was calculated using the discrete variable representation method.

Earlier investigations by high-resolution electronic spectroscopy had established accurate experimental data for the vibrational levels up to  $v=22$ , leaving open the possible existence of another level near the dissociation limit. The present theoretical calculation yielded vibrational levels up to  $v=23$ . The mean absolute deviation between the experimental and the theoretical level sets was found to be between 5 and 6 cm<sup>-1</sup>, the mean absolute deviation for the spacings between neighboring levels being 2–3 cm<sup>-1</sup>. The rotational coefficients  $B_v$  were obtained with a mean absolute deviation of 0.002 cm<sup>-1</sup>. The rotational coefficients  $D_v$ , with an average deviation of less than 10<sup>-6</sup> cm<sup>-1</sup>, are presumably more reliable than those deduced from experiment. The calculated dissociation energy was found to lie within 30 cm<sup>-1</sup> of the experimental one deduced by the spectroscopic work, for which an error bar of 8 cm<sup>-1</sup> was quoted.<sup>94</sup>

An analysis of the Dunham expansion revealed its excellent convergence for the theoretically calculated spectra and its sensitivity to the inaccuracies of the experimental spectrum. These conclusions lead to a new deduction of the spec-

troscopic constants of F<sub>2</sub> from the experimental data, which yielded new values. The deviation of the theoretical from the experimental spectroscopic constants is commensurate with deviations found for the spectral levels.

Test calculations showed that the recovery of the experimental vibrational spectrum with a mean absolute deviation of under 10 cm<sup>-1</sup> is contingent upon inclusion of all the contributions mentioned above: valence and core correlations, complete basis set extrapolation, spin-orbit coupling, and scalar relativistic contributions. Otherwise the mean error was found to increase rapidly by orders of magnitude. This importance of the higher-order corrections is in agreement with the observations of other researchers.<sup>46,50,127</sup>

Vibrational spectra of diatomic molecules probably furnish the most exacting data available for probing energetic changes along entire reaction paths. They present therefore good tests for *ab initio* methods that aim at describing reaction paths. The approach followed here has acquitted itself as up to the task.

*Note added in proof:* At about the same time as the present manuscript was submitted, a calculation of part of the vibrational spectrum of F<sub>2</sub> by Varandas has appeared in print.<sup>128</sup>

## ACKNOWLEDGMENTS

The authors thank Dr. Michael W. Schmidt for his lively interest, his stimulating critique, and his many valuable suggestions. The authors thank Dr. Branko Ruscic and Professor Robert Le Roy, Professor Hans Stauffer, and Professor Joel Tellinghuisen, for their interest and suggestions. The present work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University through the Ames Laboratory.

<sup>1</sup>L. Bytautas, T. Nagata, M. S. Gordon, and K. Ruedenberg J. Chem. Phys. **127**, 164317 (2007).

<sup>2</sup>L. Bytautas, N. Matsunaga, T. Nagata, M. S. Gordon, and K. Ruedenberg, J. Chem. Phys. **127**, 204301 (2007).

<sup>3</sup>M. Born and J. R. Oppenheimer, Ann. Phys. **84**, 457 (1927).

<sup>4</sup>P. G. Mezey, *Potential Energy Hypersurfaces* (Elsevier, New York, 1979).

<sup>5</sup>J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas, *Molecular Potential Energy Surfaces* (Wiley, New York, 1984).

<sup>6</sup>P. Pechukas, J. Chem. Phys. **64**, 1516 (1976).

<sup>7</sup>P. G. Mezey, J. Am. Chem. Soc. **112**, 3791 (1990).

<sup>8</sup>L. J. Schaad and J. Hu, J. Am. Chem. Soc. **120**, 1571 (1998).

<sup>9</sup>L. Bytautas and D. J. Klein, Int. J. Quantum Chem. **70**, 205 (1998).

<sup>10</sup>H. Eyring, J. Chem. Phys. **3**, 107 (1935).

<sup>11</sup>E. Wigner, J. Chem. Phys. **5**, 720 (1937).

<sup>12</sup>W. H. Miller, Acc. Chem. Res. **9**, 306 (1976).

<sup>13</sup>D. G. Truhlar, Annu. Rev. Phys. Chem. **35**, 159 (1984).

<sup>14</sup>T. Komatsuzaki and R. S. Berry, Proc. Natl. Acad. Sci. U.S.A. **98**, 7666 (2001).

<sup>15</sup>E. Pollak and P. Talkner, Chaos **15**, 026116 (2005).

<sup>16</sup>K. M. Kuhler, D. G. Truhlar, and A. D. Isaacson, J. Chem. Phys. **104**, 4664 (1996).

<sup>17</sup>B. Njagic and M. S. Gordon, J. Chem. Phys. **125**, 224102 (2006).

<sup>18</sup>J. M. Bowman, J. Chem. Phys. **68**, 608 (1978).

<sup>19</sup>R. A. Marcus, J. Chem. Phys. **41**, 610 (1964).

<sup>20</sup>D. K. Hoffman, R. S. Nord, and K. Ruedenberg, Theor. Chim. Acta **69**, 265 (1986).

- <sup>21</sup>D. J. Wales, *Int. J. Mod. Phys. B* **19**, 2877 (2005).
- <sup>22</sup>J. A. Pople, *Rev. Mod. Phys.* **71**, 1267 (1999).
- <sup>23</sup>R. J. Le Roy, *Mol. Spectroscop.* (Chem. Soc., London) **1**, 113 (1973).
- <sup>24</sup>W. T. Zemke, W. C. Stwalley, J. A. Coxon, and P. G. Hajigeorgiou, *Chem. Phys. Lett.* **177**, 412 (1991).
- <sup>25</sup>Z. Xie, B. J. Braams, and J. M. Bowman, *J. Chem. Phys.* **122**, 224307 (2005).
- <sup>26</sup>J. Brandão, C. Mogo, and B. C. Silva, *J. Chem. Phys.* **121**, 8861 (2004).
- <sup>27</sup>A. J. C. Varandas and P. Piecuch, *Chem. Phys. Lett.* **430**, 448 (2006).
- <sup>28</sup>R. Rydberg, *Z. Phys.* **73**, 376 (1931); O. Klein, *ibid.* **76**, 226 (1932); A. L. G. Rees, *Proc. Phys. Soc. London* **59**, 998 (1947).
- <sup>29</sup>J. Tellinghuisen, *J. Mol. Spectrosc.* **44**, 194 (1972); J. Tellinghuisen, *Comput. Phys. Commun.* **6**, 221 (1973); J. E. Blackwood, G. A. Robinson, and M. R. H. Rudge, *J. Phys. B* **33**, 1185 (2000).
- <sup>30</sup>R. J. Le Roy, Y. Huang, and C. Jary, *J. Chem. Phys.* **125**, 164310 (2006).
- <sup>31</sup>P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
- <sup>32</sup>Y. P. Varshni, *Rev. Mod. Phys.* **29**, 664 (1957).
- <sup>33</sup>A. A. Zavitsas, *J. Am. Chem. Soc.* **113**, 4755 (1991).
- <sup>34</sup>K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules, Molecular Spectra and Molecular Structure Vol. IV* (Van Nostrand Reinhold Company, New York, 1979).
- <sup>35</sup>J. F. Ogilvie, *The Vibrational and Rotational Spectrometry of Diatomic Molecules* (Academic Press, New York, 1998).
- <sup>36</sup>W. Kołos and L. Wolniewicz, *J. Mol. Spectrosc.* **54**, 303 (1975).
- <sup>37</sup>R. E. Moss and L. Valenzano, *Mol. Phys.* **101**, 2635 (2003).
- <sup>38</sup>J. Carbonell, R. Lazauskas, D. Delande, L. Hilico, and S. Kilic, *Europhys. Lett.* **64**, 316 (2003).
- <sup>39</sup>J. M. Taylor, Z.-C. Yan, A. Dalgarno, and J. F. Babb, *Mol. Phys.* **97**, 25 (1999).
- <sup>40</sup>R. Jaquet, W. Cencek, W. Kutzelnigg, and J. Rychlewski, *J. Chem. Phys.* **108**, 2837 (1998).
- <sup>41</sup>O. L. Polyansky and J. Tennyson, *J. Chem. Phys.* **110**, 5056 (1999).
- <sup>42</sup>S. Bubin and L. Adamowicz, *J. Chem. Phys.* **125**, 064309 (2006).
- <sup>43</sup>S. Bubin, L. Adamowicz, and M. Molski, *J. Chem. Phys.* **123**, 134310 (2005).
- <sup>44</sup>J. M. L. Martin, *Chem. Phys. Lett.* **303**, 399 (1999).
- <sup>45</sup>R. J. Gdanitz, *Chem. Phys. Lett.* **312**, 578 (1999).
- <sup>46</sup>O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenk, and P. J. Knowles, *Science* **299**, 539 (2003).
- <sup>47</sup>P. Piecuch, S. A. Kucharski, V. Špirko, and K. Kowalski, *J. Chem. Phys.* **115**, 5796 (2001).
- <sup>48</sup>X. Li and J. Paldus, *J. Chem. Phys.* **117**, 1941 (2002).
- <sup>49</sup>H. Müller, R. Franke, S. Vogtner, R. Jaquet, and W. Kutzelnigg, *Theor. Chem. Acc.* **100**, 85 (1998).
- <sup>50</sup>W. Cardoen and R. J. Gdanitz, *J. Chem. Phys.* **123**, 024304 (2005).
- <sup>51</sup>W. D. Laidig, P. Saxe, and R. J. Bartlett, *J. Chem. Phys.* **86**, 887 (1987).
- <sup>52</sup>X. Li and J. Paldus, *J. Chem. Phys.* **113**, 9966 (2000).
- <sup>53</sup>M. Nooijen and R. J. Le Roy, *J. Mol. Struct.: THEOCHEM* **768**, 25 (2006).
- <sup>54</sup>R. J. Gdanitz, *Chem. Phys. Lett.* **283**, 253 (1998).
- <sup>55</sup>C. Angeli, C. J. Calzado, R. Cimiraaglia, and J.-P. Malrieu, *J. Chem. Phys.* **124**, 234109 (2006).
- <sup>56</sup>C. Angeli, R. Cimiraaglia, and J.-P. Malrieu, *Chem. Phys. Lett.* **317**, 472 (2000).
- <sup>57</sup>A. D. McLean, B. Liu, and G. S. Chandler, *J. Chem. Phys.* **97**, 8459 (1992).
- <sup>58</sup>T. A. Ruden, T. Helgaker, P. Jørgensen, and J. Olsen, *J. Chem. Phys.* **121**, 5874 (2004).
- <sup>59</sup>M. Heckert, M. Kállay, D. P. Tew, W. Klopper, and J. Gauss, *J. Chem. Phys.* **125**, 044108 (2006).
- <sup>60</sup>G. E. Scuseria and H. F. Schaefer III, *Chem. Phys. Lett.* **148**, 205 (1988).
- <sup>61</sup>K. A. Peterson, R. A. Kendall, and T. H. Dunning, Jr., *J. Chem. Phys.* **99**, 9790 (1993).
- <sup>62</sup>J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **95**, 6652 (1991).
- <sup>63</sup>A. L. Wulfov, *Chem. Phys. Lett.* **263**, 79 (1996).
- <sup>64</sup>J. Mášik, I. Hubač, and P. Mach, *J. Chem. Phys.* **108**, 6571 (1998).
- <sup>65</sup>O. Živný and J. Czernek, *Chem. Phys. Lett.* **308**, 165 (1999).
- <sup>66</sup>H. Stoll, *Chem. Phys. Lett.* **376**, 141 (2003).
- <sup>67</sup>U. Louderaj, M. K. Harbola, and N. Sathiyamurthy, *Chem. Phys. Lett.* **366**, 88 (2002).
- <sup>68</sup>R. Baer and D. Neuhauser, *Phys. Rev. Lett.* **94**, 043002 (2005).
- <sup>69</sup>H.-J. Werner and P. J. Knowles, *Theor. Chim. Acta* **78**, 175 (1990).
- <sup>70</sup>C. Hampel, K. A. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992).
- <sup>71</sup>H.-J. Werner, *Mol. Phys.* **89**, 645 (1996).
- <sup>72</sup>J. Sánchez-Marín, I. Nebot-Gil, D. Maynau, and J. P. Malrieu, *Theor. Chim. Acta* **92**, 241 (1995).
- <sup>73</sup>X. Li and J. Paldus, *J. Chem. Phys.* **124**, 174101 (2006).
- <sup>74</sup>K. A. Peterson, A. K. Wilson, D. E. Woon, and T. H. Dunning, Jr., *Theor. Chem. Acc.* **97**, 251 (1997).
- <sup>75</sup>F. A. Evangelista, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **127**, 024102 (2007).
- <sup>76</sup>M. Urban and J. Noga, *Mol. Phys.* **38**, 1621 (1979); M. Urban, J. Noga, and V. Kellö, *Theor. Chim. Acta* **62**, 549 (1983).
- <sup>77</sup>J. Pittner, J. Šmýdke, P. Čársky, and I. Hubač, *J. Mol. Struct.: THEOCHEM* **547**, 239 (2001).
- <sup>78</sup>H. Moriyama, Y. Wasada-Tsutsui, M. Sekiya, and H. Tatewaki, *J. Chem. Phys.* **118**, 5413 (2003).
- <sup>79</sup>G. Das and A. C. Wahl, *J. Chem. Phys.* **56**, 3532 (1972).
- <sup>80</sup>K. Jankowski, R. Becherer, P. Scharf, H. Schiffer, and R. Ahlrichs, *J. Chem. Phys.* **82**, 1413 (1985).
- <sup>81</sup>D. C. Cartwright and P. J. Hay, *Chem. Phys.* **114**, 305 (1987).
- <sup>82</sup>J.-P. Daudey, J.-L. Heully, and J.-P. Malrieu, *J. Chem. Phys.* **99**, 1240 (1993).
- <sup>83</sup>S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, *J. Chem. Phys.* **113**, 3548 (2000).
- <sup>84</sup>V. Sychrovský, P. Čársky, and H. Lischka, *Int. J. Quantum Chem.* **76**, 185 (2000).
- <sup>85</sup>K. Kowalski and P. Piecuch, *Chem. Phys. Lett.* **344**, 165 (2001).
- <sup>86</sup>A. I. Krylov and C. D. Sherrill, *J. Chem. Phys.* **116**, 3194 (2002).
- <sup>87</sup>K. Kowalski, *J. Chem. Phys.* **123**, 014102 (2005).
- <sup>88</sup>L. Meissner, J. Gryniaków, and I. Hubač, *Mol. Phys.* **103**, 2173 (2005).
- <sup>89</sup>P. Piecuch, M. Włoch, J. R. Gour, and A. Kinal, *Chem. Phys. Lett.* **418**, 467 (2006).
- <sup>90</sup>M. Włoch, M. D. Lodriguito, P. Piecuch, and J. R. Gour, *Mol. Phys.* **104**, 2149 (2006).
- <sup>91</sup>M. Musiał and R. J. Bartlett, *J. Chem. Phys.* **122**, 224102 (2005); R. J. Bartlett and M. Musiał, *ibid.* **125**, 204105 (2006).
- <sup>92</sup>V. V. Ivanov, L. Adamowicz, and D. I. Lyakh, *Int. J. Quantum Chem.* **106**, 2875 (2006).
- <sup>93</sup>X. Li and J. Paldus, *J. Chem. Phys.* **125**, 164107 (2006).
- <sup>94</sup>J. Yang, Y. Hao, J. Li, C. Zhou, and Y. Mo, *J. Chem. Phys.* **122**, 134308 (2005).
- <sup>95</sup>E. A. Colbourn, M. Dagenais, A. E. Douglas, and J. W. Raymond, *Can. J. Phys.* **54**, 1343 (1976).
- <sup>96</sup>*Potential Energy Surfaces: Proceedings of the Mariapfarr Workshop in Theoretical Chemistry*, Lecture Notes in Chemistry Vol. 71, edited by A. F. Sax (Springer, New York, 1999); N. Sathiyamurthy, *Comput. Phys. Rep.* **3**, 1 (1985); D. Steele, E. R. Lippincott, and T. Vanderslice, *Rev. Mod. Phys.* **34**, 239 (1962).
- <sup>97</sup>R. D. Bardo and K. Ruedenberg, *J. Chem. Phys.* **59**, 5956 (1973).
- <sup>98</sup>D. F. Feller and K. Ruedenberg, *Theor. Chim. Acta* **52**, 231 (1979).
- <sup>99</sup>M. W. Schmidt and K. Ruedenberg, *J. Chem. Phys.* **71**, 3951 (1979).
- <sup>100</sup>R. C. Raffanetti, *J. Chem. Phys.* **59**, 5936 (1973).
- <sup>101</sup>R. C. Raffanetti and K. Ruedenberg, "Even-tempered exponential representations of atomic self-consistent-field wavefunctions," USAEC Research and Development Report No. 1S 3195 (Ames Laboratory, US-AEC, Iowa State University, Ames, IA, 1973).
- <sup>102</sup>X. Chu and A. Dalgarno, *J. Chem. Phys.* **121**, 4083 (2004).
- <sup>103</sup>See, e.g., L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).
- <sup>104</sup>National Institute of Standards and Technology, Physics Laboratory, Physical Reference Data, Atomic Weights and Isotopic Compositions (2005); <http://physics.nist.gov/physrefdata/compositions/>
- <sup>105</sup>Z. Bacic and J. C. Light, *J. Chem. Phys.* **85**, 4594 (1986).
- <sup>106</sup>J. C. Light, I. P. Hamilton, and J. V. Lill, *J. Chem. Phys.* **82**, 1400 (1985).
- <sup>107</sup>D. T. Colbert and W. H. Miller, *J. Chem. Phys.* **96**, 1982 (1992).
- <sup>108</sup>B. S. Garbow, J. M. Boyle, J. J. Dongarra, and C. B. Moler, *EISPACK Guide Extension Lecture Notes in Computer Science* (Springer-Verlag, New York, 1977), Vol. 51; <http://www.netlib.org/eispack/>
- <sup>109</sup>J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).
- <sup>110</sup>G. Herzberg, *Spectra of Diatomic Molecules, Molecular Spectra and Molecular Structure Vol. I* (Krieger, Malabar, 1989).
- <sup>111</sup>D. K. W. Mok, R. Neumann, and N. C. Handy, *J. Phys. Chem.* **100**, 6225 (1996).
- <sup>112</sup>R. Z. Martínez, D. Bermejo, J. Santos, and P. Cancio, *J. Mol. Spectrosc.* **168**, 343 (1994).
- <sup>113</sup>H. G. M. Edwards, D. A. Long, and R. Love, in *Advances in Raman*

- Spectroscopy*, edited by J. P. Mathieu (Heyden, London, 1972), Vol. 1, pp. 514–515.
- <sup>114</sup>W. Stricker and I. G. Hochenbleicher, *Z. Naturforsch. A* **28**, 27 (1973).
- <sup>115</sup>J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, *J. Chem. Phys.* **54**, 5165 (1971).
- <sup>116</sup>J. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.* **54**, 1952 (1958).
- <sup>117</sup>H. G. M. Edwards, E. A. M. Good, and D. A. Long, *J. Chem. Soc., Faraday Trans. 2* **72**, 984 (1976).
- <sup>118</sup>H. H. Claassen, H. Selig, and J. Shamir, *Appl. Spectrosc.* **23**, 8 (1969).
- <sup>119</sup>D. Andrychuk, *Can. J. Phys.* **29**, 151 (1951).
- <sup>120</sup>G. V. Calder and K. Ruedenberg, *J. Chem. Phys.* **49**, 5399 (1968).
- <sup>121</sup>F. Pawłowski, P. Jørgensen, J. Olsen, F. Hegelund, T. Helgaker, J. Gauss, K. L. Bak, and J. F. Stanton, *J. Chem. Phys.* **116**, 6482 (2002).
- <sup>122</sup>L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **121**, 10905 (2004).
- <sup>123</sup>L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **121**, 10919 (2004).
- <sup>124</sup>L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **121**, 10852 (2004).
- <sup>125</sup>L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **122**, 154110 (2005).
- <sup>126</sup>L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **124**, 174304 (2006).
- <sup>127</sup>S. Hirata, T. Yanai, R. J. Harrison, M. Kamiya, and P.-D. Fan, *J. Chem. Phys.* **126**, 024104 (2007).
- <sup>128</sup>A. J. C. Varandas, *Chem. Phys. Lett.* **443**, 398 (2007).