



# *Ab initio* calculation of the ro-vibrational spectrum of $\text{H}_2\text{F}^+$

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## ABSTRACT

An *ab initio* study of the rotation-vibrational spectrum of the electronic ground state of the (gas-phase) fluoronium ion  $\text{H}_2\text{F}^+$  is presented. A new potential energy surface (PES) and a new dipole moment surface (DMS) were produced and used to compute rotation-vibrational energy levels, line positions and line intensities. Our computations achieve an accuracy of  $0.15\text{ cm}^{-1}$  for the fundamental vibrational frequencies, which is about 50 times more accurate than previous *ab initio* results. The computed room-temperature line list should facilitate the experimental observations of new  $\text{H}_2\text{F}^+$  lines, in particular of yet unobserved overtone transitions. The  $\text{H}_2\text{F}^+$  molecular ion, which is isoelectronic to water, has a non-linear equilibrium geometry but a low-energy barrier to linearity at about  $6000\text{ cm}^{-1}$ . As a result the effects of so-called quantum monodromy become apparent already at low bending excitations. An analysis of excited bends in terms of quantum monodromy is presented.

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## 1. Introduction

The fluoronium ion  $\text{H}_2\text{F}^+$  possesses at least three points of interest. First, fluoronium is expected to be produced in the interstellar medium by reaction of  $\text{H}_3^+$  with HF [1];  $\text{H}_3^+$  [2–5], hydrogen fluoride HF [6,7] and also  $\text{H}_2\text{Cl}^+$  [8] have already been detected in space, but not  $\text{H}_2\text{F}^+$ . It is hoped that a more detailed knowledge of its spectrum might ease its future detection.

Second, the energy level structure of fluoronium is an interesting example of so-called quantum monodromy [9–11]. While the general topology of the  $\text{H}_2\text{F}^+$  potential energy surface (PES) is similar to the one of water ( $\text{H}_2\text{F}^+$  has a bent equilibrium geometry with  $r_e = 0.96\text{ Å}$  and  $\theta_e = 112^\circ$ ) the energy required to reach linear geometries (the so-called barrier to linearity) is only about  $6000\text{ cm}^{-1}$  compared to about  $11\,100\text{ cm}^{-1}$  for water [12]. This low-energy barrier to linearity leads to the appearance of so-called quantum monodromy already for low bending quantum number  $\nu_2$ ; we will show in this paper that the effect of quantum monodromy occurs in  $\text{H}_2\text{F}^+$  starting from  $\nu_2 = 5$  and should be much easier to observe than in the case of water, for which it becomes apparent only for  $\nu_2 = 9$  [13,14].

Third, by virtue of its small number of electrons fluoronium is an interesting benchmark system for testing the accuracy

achievable with highest-level electronic structure methods and as a result it has been the subject of a fairly large number of theoretical calculations [15–32].

In Ref. [33] we presented *ab initio* calculations of the spectrum of various water isotopologues (energy levels with energies up to  $15\,000\text{ cm}^{-1}$  and up to rotational quantum number  $J = 20$ ) with an unprecedented accuracy of  $0.10\text{ cm}^{-1}$  and we conjectured that it should be possible to obtain comparable accuracy for other molecules containing 10 electrons such as  $\text{NH}_3$ ,  $\text{H}_3\text{O}^+$  and  $\text{CH}_4$ . Because these molecules are made up by more atoms both the calculation of their PESs and the solution of the nuclear motion problem require considerably more computer resources than is the case for triatomics. In this context  $\text{H}_2\text{F}^+$  becomes an ideal candidate to test our theoretical approach with reasonable computational effort.

From the experimental point of view the spectrum of  $\text{H}_2\text{F}^+$  is not very well studied, no doubt in part because of the difficulties associated with its extreme chemical reactivity. Only the rotational spectrum [34,35] and the spectrum of the three fundamental bands have been observed [1,36,37].

The paper is organized as follows. Section 2 describes the details of the electronic structure calculations used to produce our very high quality PES and dipole moment surface (DMS). In Section 3 we use the PES and DMS to solve the nuclear motion problem and calculate rovibrational energy levels, line positions and line intensities. We present a line list which may be used for the identification of yet unobserved  $\text{H}_2\text{F}^+$  overtone transitions. In Section 4

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we present an analysis of the effect of quantum monodromy in  $\text{H}_2\text{F}^+$ . Finally, Section 5 concludes the paper.

## 2. Electronic structure calculations

### 2.1. General strategy

In a recent study Gutlé and Coudert [32] produced an *ab initio* potential energy surface (PES) based on CCSD(T) (coupled cluster single, double and perturbative triple excitations), the cc-pwCV5Z basis set for fluorine and cc-pVQZ for hydrogen; this PES was produced on the basis of a dense grid of 8864 geometry points with energies up to  $20\,000\text{ cm}^{-1}$ . Relativistic and other smaller corrections were neglected. These authors also semi-empirically modified the *ab initio* PES to fit the known experimental data and used it to compute rotational-vibrational (rovibrational) energy levels (up to  $10\,000\text{ cm}^{-1}$  and with angular momentum  $J \leq 5$ ); a small line list of 4878 strong lines was also produced by using a dipole moment surface (DMS) taken from Ref. [29].

The accuracy of the *ab initio* PES reported in Ref. [32] in reproducing the three known fundamental vibrational frequencies is of about  $10\text{ cm}^{-1}$ ; by contrast in this study we aim to and achieve with an *ab initio* procedure a much higher accuracy of about  $0.15\text{ cm}^{-1}$ .

To do this we apply the same calculation scheme we used in Ref. [33] to achieve extremely good accuracy for *ab initio* ro-vibrational energy levels of the water molecule (errors for the three fundamental vibrations of  $\approx 0.65\text{ cm}^{-1}$  when neglecting non-adiabatic corrections and of  $\approx 0.11\text{ cm}^{-1}$  when including them). The scheme introduced in that study comprises 11 aspects which should be taken into account when aiming at sub- $\text{cm}^{-1}$  accuracy in rovibrational energy levels and follows the spirit of extrapolation approaches such as focal-point analysis [38,39] or the HEAT [40,41] and Weizmann- $n$  [42] models. Our scheme is expected to be immediately applicable to closed-shell molecules made up by hydrogen and second-row atoms.

The components we identified, in approximately decreasing order of magnitude are:

1. A main, non-relativistic Born–Oppenheimer component based on multireference configuration interaction (MRCI) using the full-valence complete active space reference space and the aug-cc-pCV6Z basis set [43–45].
2. A basis set incompleteness error correction based on basis set extrapolation [46–48] using the aug-cc-pCV6Z and aug-cc-pCV5Z basis sets. As is shown in [49] a(56)Z basis set extrapolation reduces the aug-cc-pCV6Z basis set incompleteness error by a factor about 3 and provides a realistic way to calculate an extremely accurate Born–Oppenheimer (BO) part of the PES.
3. We found that sub- $\text{cm}^{-1}$  *ab initio* accuracy requires computing energies on a grid of points denser than usually done. This high density of points is necessary in practice to avoid spurious oscillations introduced by the fitting. An extreme example of this situation was reported in Ref. [50,51]; in that study two PESs for the  $\text{H}_3^+$  molecular ion were compared, one based on a ultra-dense grid of 42,000 points and a second one based on a coarse grid of 69 points [52]. Both PESs were based on *ab initio* calculations with an intrinsic accuracy of at least  $0.02\text{ cm}^{-1}$ . An analysis of the two PESs shows differences (in regions within the range covered by the grid points) of up to  $20\text{ cm}^{-1}$ , so that the PES based on the coarse grid could not represent consistently the accuracy of the underlying *ab initio* points. In the case of triatomic molecules we estimate that a fairly complete coverage of the PES (not

covering the near-dissociation region) should require 2000–3000 grid points. An even denser grid is beneficial for the DMS [53].

4. The residual error in the electron correlation treatment performed at step 1 must be corrected. This can be achieved by performing calculations with active spaces larger than the full-valence one. Some experimentation may be required when choosing the enlarged reference space.
5. An adiabatic Born–Oppenheimer diagonal correction (BODC) surface has to be calculated. Experience shows (e.g. [54,55]) that shifts of energy levels due to the BODC are likely to be of the order of  $1\text{ cm}^{-1}$  or larger for molecules containing hydrogen atoms.
6. A scalar-relativistic (i.e., spin-independent) correction surface based on the Breit–Pauli Hamiltonian (which reduces to the mass-velocity one-electron Darwin operator for spin singlet electronic states) [56,57] or alternatively on the Douglas–Kroll–Hess Hamiltonian [58].
7. A higher-level relativistic correction surface based on the Dirac–Coulomb–Gaunt or Dirac–Coulomb–Breit Hamiltonian [59–61].
8. A surface modeling quantum electrodynamics (QED) corrections [59,62], which has been shown to introduce shifts of more than  $1\text{ cm}^{-1}$  to water energy levels, should be included. For molecules containing light atoms ( $Z \leq 10$ ) this correction can be very conveniently obtained by simple scaling of the Darwin operator [62–64]; for molecules containing heavier atoms the accuracy of the scaling scheme is at present unknown.
9. Vibrational nonadiabatic corrections have to be implemented. The simplest way to do this is to use scaled vibrational reduced masses instead of nuclear ones, as done for  $\text{H}_3^+$  in [52] following Bunker and Moss' model [65]. A more sophisticated approach was presented by Schwenke in Ref. [66] and was adopted in a simplified form in Ref. [33] to reach sub- $0.1\text{ cm}^{-1}$  accuracy for water.
10. Finally, rotational nonadiabatic corrections should be included. As shown in [65] these corrections are directly linked to the so-called rotational  $g$ -factor [67,68], which can be computed *ab initio* in a relatively standard manner [69].
11. For spin-singlet molecules the effect of spin–orbit interaction on ro-vibrational energy levels is usually negligible apart possibly from a few very high-energy ones approaching the dissociation threshold. For such levels off-diagonal spin–orbit coupling [70,71] to low-lying electronic triplet states may introduce shifts which may be of the order of  $1\text{ cm}^{-1}$  if the triplet states are nearly degenerate with the ground singlet one.

In the present study we do not consider nonadiabatic corrections (beyond using atomic masses for the nuclear motion problem); from our experience with water we estimate that such effects influence the fundamental vibration frequencies (the only ones experimentally known) by less than  $0.1\text{ cm}^{-1}$ . We also neglect spin–orbit coupling effects, which should be completely negligible for  $\text{H}_2\text{F}^+$ . Note that the lowest-dissociation channel of  $\text{H}_2\text{F}^+$  leads to  $\text{HF} + \text{H}^+$ , and as HF has a ground state singlet state there are no triplet states nearly degenerate with the ground state.

### 2.2. Technical Details

The main computations were performed using MOLPRO [72,73] at the all-electron, Davidson corrected (+Q) internally-contracted multireference configuration interaction (IC-MRCI) level [74,75],

using the aug-cc-pCVnZ ( $n = 5$  and  $6$ ) correlation-consistent basis sets [43,44]. The Davidson correction was computed using the fixed reference (see the MOLPRO manual or Ref. [74] for an explanation). The reference space (of complete active space type) used is larger than the full valence one and is the same 8-electron, 10-orbital one used in Refs. [33,53] for the water molecule.

Denoting with  $r_1$  and  $r_2$  the two F–H bond lengths and with  $\theta$  the H $\ddot{\text{F}}$ H bond angle, we initially computed energies on a grid of about 3000 random points; of these we selected for fitting a subset of 1210 points with energies up to  $17,000 \text{ cm}^{-1}$ . Basis set extrapolation was based on the formula  $E_n = E_\infty + A/(n + \frac{1}{2})^4$ , which is shown to work very well for the calculation of atomization energies [46–48] and also for the  $\text{H}_2$  and  $\text{H}_3^+$  molecules [64].

The *ab initio* points were fitted to the same analytical expression used for the water molecule [33]. A few points with large fitting residuals (most likely because of convergence problems in the electronic structure calculations) were excluded from the fit and our final PES reproduced the *ab initio* points with a fitting standard deviation of  $0.7 \text{ cm}^{-1}$ . This surface was augmented with a relativistic correction and an adiabatic correction, which were fitted separately. This nonrelativistic PES leads to an equilibrium geometry  $r_e = 0.9601 \text{ \AA}$  and  $\theta = 112.6^\circ$ . These values are in good agreement with the experimentally-derived ones [1]  $r_e = 0.9608(6) \text{ \AA}$  and  $\theta = 112.2(2)^\circ$ .

A relativistic correction surface was produced using the expectation values of the mass-velocity one-electron Darwin operator (MVD1) computed with the MRCI/aug-cc-pCV6Z wave function. The adiabatic correction surface was computed using the program CFour [76] and all-electron coupled cluster singles and double excitations (CCSD) [77] in the aug-cc-pCVDZ basis set. The higher-order relativistic correction surface was computed using the program DIRAC [78] and four-component Dirac-Coulomb-Gaunt Hamiltonian using CCSD(T) [77] and the aug-cc-pCVDZ basis set. Finally, the QED correction surface was obtained by scaling the expectation value of the one-electron Darwin operator by the factor 0.02257, taken from the fourth column of table II of Ref. [63] (value relative to fluorine atom).

### 3. Calculation of the rovibrational spectrum

Using the nonrelativistic, relativistic and adiabatic PESs described in the previous section we calculated energy levels of  $\text{H}_2\text{F}^+$  using the DVR3D program suite [79].

#### 3.1. Technical details

We used Radau internal coordinates, bisector embedding, Morse-like oscillator basis functions for the radial coordinates and Legendre polynomials for the angle coordinate; the Morse-like basis used  $r_e = 2.05 a_0$ ,  $D_e = 0.25 E_h$  and  $\omega_e = 7 \text{ mE}_h$ , we used 20 DVR grid points in each radial coordinate and 40 angular DVR grid points. The size of the matrix was truncated at 1500 at the first step of the calculation (program DVR3DRJZ). We used the following (nuclear) masses:  $m(^1\text{H}) = 1.007276 \text{ u}$  and  $m(^{19}\text{F}) = 18.998403 \text{ u}$ . At the second step of the calculation (program ROTLEV3B) the matrix truncation parameter IBASS was set to  $600 \times (J + 1)$ . Energy levels were computed for  $J \leq 6$ .

#### 3.2. Results for vibrational and rotational energy levels

We report in Table 1 vibrational ( $J = 0$ ) energy levels up to  $10\,000 \text{ cm}^{-1}$  computed using the Born–Oppenheimer (BO) non-relativistic potential energy surface as well as the energy level shifts due to the Born–Oppenheimer diagonal correction,

**Table 1**

Predicted vibrational ( $J = 0$ ) energy levels for  $\text{H}_2\text{F}^+$  using the non-relativistic Born–Oppenheimer (BO) potential energy surface and net effect of the Born–Oppenheimer diagonal correction (BODC), scalar-relativistic effects (REL) and QED correction surfaces to the BO values. All energies are in  $\text{cm}^{-1}$ .

$\nu_1$	$\nu_2$	$\nu_3$	BO	BODC	REL	QED
0	1	0	1368.959	−1.142	2.703	−0.165
0	2	0	2672.674	−2.323	6.072	−0.372
0	0	1	3337.970	−0.845	−2.617	0.136
1	0	0	3352.102	−1.304	−2.409	0.127
0	3	0	3888.907	−3.643	10.769	−0.660
0	1	1	4678.271	−1.969	−0.034	−0.021
1	1	0	4694.967	−2.440	0.284	−0.037
0	4	0	4977.234	−5.113	17.061	−1.041
0	2	1	5957.159	−3.125	3.168	−0.216
1	2	0	5952.291	−4.633	9.676	−0.671
0	5	0	5998.256	−4.625	12.157	−0.672
0	0	2	6506.921	−2.094	−4.841	0.251
1	0	1	6512.390	−2.156	−4.830	0.251
2	0	0	6702.740	−2.268	−5.024	0.264
0	6	0	7073.500	−5.169	12.245	−0.747
0	3	1	7155.093	−4.398	7.576	−0.485
1	3	0	7179.208	−4.940	8.653	−0.545
0	1	2	7819.752	−3.195	−2.316	0.098
1	1	1	7825.801	−3.271	−2.285	0.096
2	1	0	8017.730	−3.408	−2.381	0.103
0	4	1	8233.935	−5.852	13.757	−0.856
1	4	0	8230.453	−6.204	13.575	−0.846
0	7	0	8361.285	−5.112	8.657	−0.534
0	2	2	9070.863	−4.380	0.999	−0.104
1	2	1	9076.292	−4.458	1.145	−0.114
1	5	0	9209.338	−6.485	12.848	−0.819
0	5	1	9213.661	−6.523	15.752	−0.965
2	2	0	9284.565	−4.893	3.198	−0.205
0	0	3	9500.485	−3.224	−6.935	0.356
1	0	2	9501.041	−3.240	−6.930	0.356
0	8	0	9736.250	−5.011	4.479	−0.289
2	0	1	9856.619	−2.928	−7.534	0.393
3	0	0	9902.006	−3.766	−7.242	0.379

scalar-relativistic and QED effects. Scalar-relativistic effects constitute the largest correction, ranging in magnitude between  $-7.5$  and  $+17 \text{ cm}^{-1}$ ; they generally raise the energy of bends by about  $2.7 \times \nu_2 \text{ cm}^{-1}$  and lower both symmetric and asymmetric stretches by about  $2.4 \text{ cm}^{-1}$  for each stretching quanta. The adiabatic BODC correction leads to shifts between  $-0.8$  and  $-6.5 \text{ cm}^{-1}$  and always leads to a lowering of the energy levels (approximately  $1.2 \text{ cm}^{-1}$  for each vibrational quanta). Finally, the QED correction surface leads to shifts which range between  $-1.0$  and  $0.4 \text{ cm}^{-1}$  and which are strongly anticorrelated with the relativistic ones, being approximately equal to the relativistic shifts times  $-0.06$ . This happens because for  $\text{H}_2\text{F}^+$  the mass-velocity and the Darwin contributions (whose sum gives the full relativistic correction) are approximately proportional to one another, and the QED correction is taken in our scheme as exactly proportional to the Darwin term.

Note that the general trends outlined above are subject to some exceptions, especially for combination modes and high bends with  $\nu_2 \geq 5$ ; this is to be expected, as energy levels corresponding to high bends cross the barrier to linearity and the corresponding vibrational wave functions undergo a qualitative change (see Section 4).

In Table 2 we report for the same set of energy levels a comparison with the experimental values for the fundamental bands and with the levels by Gutlé and Coudert [32]; as a result of the semi-empirical optimization process employed in Ref. [32] we expect the accuracy of their energy levels to be high (better than  $0.1 \text{ cm}^{-1}$ ) for the lowest energy levels and to progressively degrade at higher energies.

In Table 2 we denoted as PES1 the potential energy surface obtained as the sum of the BO one and of the relativistic and

**Table 2**

Vibrational ( $J = 0$ ) energy levels for  $\text{H}_2\text{F}^+$  computed with various levels of theory compared with the semi-empirical ones by Gutlé and Coudert [32] (labeled GT12) and with experimental values for the fundamental vibrations. The column labeled PES1 includes the nonrelativistic Born–Oppenheimer PES, the adiabatic correction and the relativistic correction surface based on the Dirac–Coulomb–Gaunt Hamiltonian. The column labeled PES2 further include quantum electrodynamics corrections. The columns labeled  $\Delta_{\text{obs}}$  report the differences  $E(\text{experiment}) - E(\text{this work})$  while  $\Delta_{\text{GT12}}$  are the corresponding differences with GT12 values. The experimental values are taken from table I of Ref. [1] and are  $\nu_1 = 3348.7284(12) \text{ cm}^{-1}$ ,  $\nu_2 = 1370.52356(67) \text{ cm}^{-1}$  and  $\nu_3 = 3334.68783(79) \text{ cm}^{-1}$ ; note that the value for  $\nu_1$  reported in Ref. [1] for  $\nu_1$  is misspelt as  $3378.7284 \text{ cm}^{-1}$  (compare with the previous experimental  $3348.7078(36) \text{ cm}^{-1}$  from Ref. [37]).

$\nu_1$	$\nu_2$	$\nu_3$	GT12	PES1	PES2			
					$\Delta_{\text{obs}}$	$\Delta_{\text{GT12}}$	$\Delta_{\text{obs}}$	$\Delta_{\text{GT12}}$
0	1	0	1370.5	1370.52	0.00	0.0	1370.36	0.16
0	2	0	2676.7	2676.43		0.3	2676.06	0.6
0	0	1	3334.7	3334.51	0.18	0.2	3334.64	0.05
1	0	0	3348.8	3348.39	0.34	0.4	3348.52	0.21
0	3	0	3897.0	3896.05		0.9	3895.40	1.6
0	1	1	4675.9	4676.27		−0.4	4676.25	−0.4
1	1	0	4692.8	4692.82		0.0	4692.78	0.0
0	4	0	4990.6	4989.20		1.4	4988.17	2.4
0	2	1	5956.3	5957.21		−0.9	5957.09	−0.8
1	2	0	5963.2	5957.64		5.6	5957.00	6.2
0	5	0	6003.4	6005.45		−2.1	6004.66	−1.3
0	0	2	6500.1	6499.99		0.1	6500.24	−0.1
1	0	1	6504.7	6505.39		−0.7	6505.64	−0.9
2	0	0	6697.0	6695.45		1.6	6695.71	1.3
0	6	0	7095.1	7080.54		14.6	7079.78	15.3
0	3	1	7157.1	7158.29		−1.2	7157.81	−0.7
1	3	0	7179.0	7182.93		−3.9	7182.39	−3.4
0	1	2	7813.9	7814.24		−0.3	7814.34	−0.4
1	1	1	7818.7	7820.23		−1.5	7820.33	−1.6
2	1	0	8012.7	8011.94		0.8	8012.05	0.6
0	4	1	8240.3	8241.87		−1.6	8241.02	−0.7
1	4	0	8243.3	8237.85		5.4	8237.02	6.3
0	7	0	8380.8	8364.79		16.0	8364.24	16.6
0	2	2	9067.1	9067.50		−0.4	9067.40	−0.3
1	2	1	9071.5	9072.98		−1.5	9072.88	−1.4
1	5	0	9221.2	9215.81		5.4	9215.02	6.2
0	5	1	9221.3	9222.86		−1.6	9221.88	−0.6
2	2	0	9278.3	9282.73		−4.4	9282.49	−4.2
0	0	3	9490.9	9490.37		0.5	9490.73	0.2
1	0	2	9491.1	9490.87		0.2	9491.23	−0.1
0	8	0	9774.2	9735.69		38.5	9735.39	38.8
2	0	1	9848.2	9846.14		2.1	9846.53	1.7
3	0	0	9891.9	9891.00		0.9	9891.38	0.5

BODC corrections; PES2 further includes the QED correction surface. As it can be seen from Table 2 our fundamental band origins computed with PES2 agree with the experimental values to better than  $0.15 \text{ cm}^{-1}$  on average.

Discrepancies between our *ab initio* calculations and the ones by Guttle and Coudert increase for highly excited bending levels and become particularly large for high bends. We believe that our predictions of highly excited bending levels of  $\text{H}_2\text{F}^+$  are more reliable than the ones due to Guttle and Coudert [32] because of the high level of our *ab initio* treatment. It is reasonable to suppose that our predicted excited bends have an accuracy not much worse to the one achieved for water [33], for which excited bends were predicted with sub-wavenumber accuracy.

On the other hand, since  $\text{H}_2\text{F}^+$  is very floppy, the predictions of the fitted PES [32], where only first fundamental bending state is included in the fit, may extrapolate poorly at higher bending quanta. In conclusion, we think that the large  $38 \text{ cm}^{-1}$  discrepancy for the  $\nu_2 = 8$  level of the Ref. [32] (see Table 2) is due to the inaccuracy of the fitted PES of Ref. [32].

We compare in Table 3 rotationally excited energy levels up to  $J = 6$  in the ground (000) vibrational band with experimental values. In absolute terms the computed rotationally excited energy

**Table 3**

Rotational energy of  $\text{H}_2\text{F}^+$  in the ground (000) vibrational band. The column labeled 'obs' reports experimentally-derived values from Ref. [32]. The column labeled PES2 includes the nonrelativistic Born–Oppenheimer PES, the adiabatic correction, the relativistic correction surface based on the Dirac–Coulomb–Gaunt Hamiltonian and quantum electrodynamics corrections. The column labeled  $\Delta$  reports the difference  $E[32] - E(\text{this work})$ .

$J$	$K_a$	$K_c$	Obs	PES2	$\Delta$
1	0	1	21.96	21.97	0.00
1	1	1	43.54	43.53	0.01
2	0	2	65.4	65.41	−0.01
2	1	1	95.07	95.07	0.00
2	1	2	83.67	83.67	0.00
2	2	1	158.89	158.85	0.04
3	0	3	129.4	129.42	−0.02
3	1	2	166.25	166.27	−0.02
3	1	3	143.56	143.57	−0.01
3	2	2	224.84	224.82	0.02
4	0	4	212.84	212.86	−0.02
4	1	3	260.4	260.42	−0.02
4	1	4	222.89	222.90	−0.01
4	2	2	318.7	318.70	0.00
4	2	3	312.3	312.29	0.01
4	3	2	426.98	426.92	0.06
5	0	5	314.7	314.72	−0.02
5	2	3	434.7	434.72	−0.02
5	2	4	420.88	420.88	0.00
5	3	2	539.03	538.99	0.04
5	3	3	538.08	538.04	0.04
6	1	5	514.35	514.41	−0.06
6	3	3	673.95	673.92	0.03

levels are very accurate, with errors in the range  $0.01$  to  $0.05 \text{ cm}^{-1}$ . More specifically, computed energy levels are slightly too large, and in the range investigated the systematic error grows linearly with  $J$  and is approximately given by  $0.009 \times (J - 1) \text{ cm}^{-1}$ . It is likely that the introduction of rotational non-adiabatic corrections would improve agreement with experiment even further.

### 3.3. Line intensities

We produced a new  $\text{H}_2\text{F}^+$  dipole moment surface (DMS) using the expectation value dipoles produced by MOLPRO during our main MRCI/aug-cc-pCV6Z energy calculation. It is known that dipole moments computed by expectation values with approximate wave functions are often less accurate than dipoles computed (at the same level of electronic structure theory) as derivative of the energy, considered as a function of an external, uniform electric field, for zero field strength [80]. We chose not to use energy derivative dipoles as their calculation requires four times as much computations and is worthwhile only when very high accuracy ( $< 2\%$ ) is needed.

The *ab initio* dipole points were fitted using the functional form used for the LTP2011 water DMS by Lodi et al. [53]. The fit included 224 parameters and produced a fitting standard deviation of  $5 \times 10^{-6}$  a.u. for both components. The resulting DMS was used to compute a room-temperature (296 K) spectrum of  $\text{H}_2\text{F}^+$  up to  $J = 6$ . An overview of the spectrum is presented as Fig. 1.

The complete linelist, which could be used for the identification of the new lines, is provided in the supplementary material. The linelist contains the frequencies and intensities of the lines up to  $J = 6$  calculated at the room temperature. The variational calculations do not provide automatically the labeling of the energy levels with approximate quantum numbers  $K_a, K_c, \nu_1, \nu_2$  and  $\nu_3$ . Only exact quantum number  $J$  is given. So we provided the energy levels involved in the linelist with the labels by these quantum numbers only for the lower levels. Upper energy levels are labeled by  $J$ , orto-para symmetry and a counting number within each symmetry block.



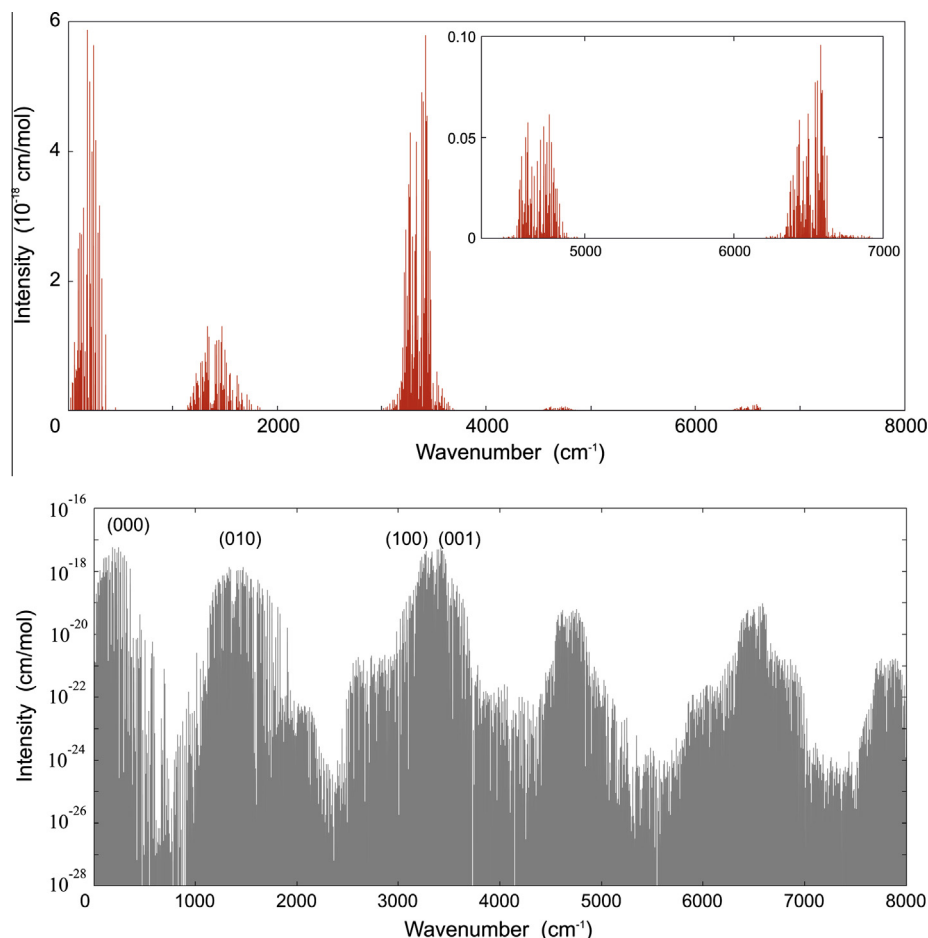


Fig. 1. Plots of our calculated 296 K absorption spectrum for  $\text{H}_2\text{F}^+$  with lines up to  $J = 6$ . Upper plot: linear scale in intensities. Lower plot: logarithmic scale in intensities.

#### 4. Quantum monodromy

The name monodromy (meaning ‘once round’) was first used in the late 1860s in the context of axiomatization of geometry [81] and indicates the study of how mathematical objects behave when transported around some kind of singularity along a closed circuit. Such usage is well established in mathematics and mathematical physics [82,83], e.g. in the theory of differential equations [84] or in complex analysis. Starting from the 1970s several authors [85–87] have studied classical mechanics systems in terms of their monodromy properties in phase space; similar analysis were subsequently carried out for quantum mechanical model systems [88,89]. Starting from the late 1990s several studies of the implications of quantum monodromy in existing atomic and molecular systems have been carried out [13,14,90–96]; see also [9–11,97,98] and in particular [93] for general reviews of quantum monodromy.

For quasilinear molecules or for molecules with bent equilibrium structure but a low barrier to linearity it has been shown [93,99] that there is no smooth, globally valid set of quantum numbers which can be applied to the entire spectrum. In triatomic molecules with a linear equilibrium geometry the bending levels are usually labeled by the quantum numbers  $[\nu_2^{\text{linear}}, l]$ , whereas in molecules with a non-linear equilibrium geometry bends are labeled with the quantum numbers  $[\nu_2^{\text{bend}}, K_a]$  [100]. These two labeling schemes are connected by the formulae

$$\begin{aligned} \nu_2^{\text{linear}} &= 2\nu_2^{\text{bend}} + K_a \\ \nu_2^{\text{bend}} &= \frac{1}{2}(\nu_2^{\text{linear}} - |l|) \end{aligned} \quad (1)$$

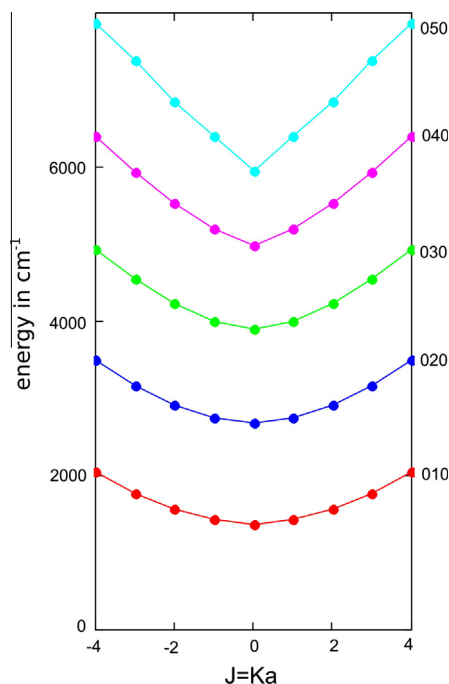
Monodromy provides a test of the smoothness of either of these individual labeling schemes [99].

Our variational calculations do not directly use approximate quantum numbers such as  $K_a$  and  $K_c$  as only exact quantum numbers ( $J$ , ortho/para label and parity) are assigned to levels. However, there are many well-established techniques for assigning approximate quantum numbers [101–105]; in particular, as we are dealing with relatively low-energy states, labeling of the  $\text{H}_2\text{F}^+$  was performed unambiguously by matching computed energy levels with the ones predicted by the rigid rotor/harmonic oscillator model. Computed energy levels along with exact and approximate quantum numbers are provided in the [supplementary material](#).

In  $\text{H}_2\text{F}^+$  monodromy leads to a change in the structure of the energy levels as a function of  $\nu_2, J$  and  $K$ . The monodromy point is the energy at which the change from the structure of bend molecule to the structure of linear molecule occurs and corresponds to the barrier to linearity, for which our most complete *ab initio* PES (labeled PES2 in [Tables 2 and 3](#)) predicts a value of  $6281 \text{ cm}^{-1}$ .

Such transition can be identified graphically by plotting energy levels as functions of the quantum number  $K_a$  (and fixing  $J = K_a, K_c = 0$ ) (see [Fig. 2](#)). For energies below the monodromy points energy levels have a quadratic dependence  $K_a^2$  while above the monodromy points the dependence is linear of the  $|K_a|$  type. One can see from the plot that the transition happens between  $\nu_2 = 4$  and  $\nu_2 = 5$ . The same effect has already been experimentally confirmed in the water molecule [14], in which case it takes place at much higher bending excitations ( $\nu_2 > 9$ ).

The low barrier to linearity of  $\text{H}_2\text{F}^+$  has another interesting aspect. It results in an extreme floppiness of the molecule, which leads in turn to poor convergence of effective Hamiltonians based



**Fig. 2.** Computed  $\text{H}_2\text{F}^+$  energy levels for pure bends  $(0, \nu_2, 0)$  having  $K_a = J$  and  $K_c = 0$  plotted as a function of  $J$ . States are plotted also for negative  $J$  to underline the change in the behavior about the level with  $J = 0$  as the degree of bending excitation is increased.

on perturbation theory (PT) [106]. The use of divergent series summation techniques was demonstrated to be effective for high  $K_a$  energy levels of water [106,107] and methods of PT summation have been successfully used for the vibrational levels calculations of various triatomic molecules [108]. A natural extension of these methods to the calculation of rotation-vibration levels would require benchmark data on molecules with a slowly convergent PT expansion and the  $\text{H}_2\text{F}^+$  molecular ion could constitute an interesting system for this kind of studies.

## 5. Conclusions

We have calculated a new *ab initio* potential energy surface (PES) and dipole moment surface (DMS) for the fluoronium molecular ion  $\text{H}_2\text{F}^+$ . As described in Section 2 we identify 11 steps necessary for achieving sub- $\text{cm}^{-1}$  accuracy, which include high level electron correlation, relativistic and non-adiabatic corrections. Not all of these terms were taken into account in this study, but nevertheless the accuracy of our calculated rovibrational line position ( $J = 0$  to  $J = 6$ ) is of the order of  $0.15 \text{ cm}^{-1}$  for the fundamental bands, that is more than 50 times higher than in the previous *ab initio* calculations [32]. The newly computed PES and DMS were used to produce a room-temperature linelist, which is made available in the [supplementary material](#) and, it is hoped, will help experimentalists to observe new overtone transition. These results reinforce the hope that other molecules with around 10 electrons (comprising only second-row atoms or hydrogen) could be described to the same accuracy using an analogous approach. In particular, this includes  $\text{NH}_3$ ,  $\text{H}_3\text{O}^+$  and  $\text{CH}_4$ .

The  $\text{H}_2\text{F}^+$  molecular spectrum exhibits the same qualitative quantum monodromy effect as already observed in the water molecule [14]. However, in  $\text{H}_2\text{F}^+$  this effect takes place at much lower values of the bending excitation, than in water. The results presented in this paper are expected to be much more accurate than previous ones (especially for highly excited bending states)

and could aid the experimental observation of this interesting qualitative effect.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2015.07.002>. These data include MOL files and InChIKeys of the most important compounds described in this article.

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