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Andrei V Nikitin, Michael M. Rey, Iana S Chizhmakova, Vladimir G. Tyuterev. First Full-Dimensional Potential Energy and Dipole Moment Surfaces of SF₆. *Journal of Physical Chemistry A*, 2020, 124 (35), pp.7014-7023. <10.1021/acs.jpca.0c02733>. <hal-03045937>

HAL Id: hal-03045937

<https://hal.science/hal-03045937v1>

Submitted on 8 Dec 2020

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FIRST FULL-DIMENSIONAL POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES OF SF₆

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Running Head: potential energy surface and dipole moment surface of SF₆

Keywords: SF₆, ab initio, potential energy surface, dipole moment surface, low resolution spectra.

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ABSTRACT

A 15-dimensional analytical form for the potential energy and dipole moment surfaces of the SF₆ molecule in the ground electronic state is obtained using ab initio methods. In order to calculate the equilibrium S-F distance, we applied coupled cluster CCSD(T) method and several versions of the correlation consistent basis sets - from valence triple-zeta (VTZ) and augmented valence triple-zeta (AVTZ) to core-valence quadruple-zeta (CVQZ) with Douglas-Kroll (DK) relativistic corrections that provided good agreement with empirical equilibrium value. Ab initio electronic energies on 15D grids of nuclear geometries are computed using CCSD(T) method with VTZ and CVQZ-DK basis sets. The analytical representation of the potential energy surface is determined through an expansion in symmetry adapted products of non-linear coordinates up to the 5-th order. The influence of additional redundant coordinates on the quality of the fit was investigated. Parameters of full dimensional dipole moment surfaces are determined up to the 4-th order expansion in normal mode coordinates. For validation of ab initio results, the fundamental vibration frequencies and absorption cross-sections of the principal sulfur hexafluoride isotopologue are calculated giving good agreement with cold (180 K) and room temperature (296 K) experimental spectra. Absorption cross-sections calculated from our preliminary line list agree much better with these observations than the simulations using SF₆ line-by-line lists constructed from effective models included in currently available spectroscopic databases.

Keywords: Potential Energy Surface, Dipole moment surface, SF₆, Octahedral Group octahedron

Introduction

Investigation of electronic structure and radiative properties of high octahedral symmetry sulfur hexafluoride (SF₆) molecule are of interest both for the theory [1,2,3] and for applications in many domains of industry and medicine. Because of strong absorption bands in the atmospheric transparency windows, SF₆ is a powerful greenhouse gas with the global warming potential (GWP500) by 29300 times larger than that of CO₂ [4]. At present, the sulfur hexafluoride atmospheric concentration is yet small, but SF₆ is one of the most stable gaseous chemicals with an atmospheric life time of 3200 years [5]. According to the conclusions of Earth System Research Laboratory Global Monitoring Division [6], the SF₆ concentration increased from 3.5ppt (1995) to 9.5ppt (2018). A rapid increase of the SF₆ concentration and its long atmospheric life time might result in a considerable accumulation of SF₆ in the troposphere. Thus, in future, sulfur hexafluoride may play an important role in the climate global changing. The radiative properties of SF₆ were insufficiently studied up to now. Because of a relatively low-frequency vibrations [7], the Boltzmann population of the excited vibrational levels appears to be significant. Thus, the ‘hot bands’ corresponded to transitions between excited vibrational states produce a considerable contribution to IR absorption even at room temperature. The ro-

vibrational spectra are quite complex and crowded making it difficult to identify isolated lines in experimentally recorded absorption samples. Only few vibrational bands of SF₆ within limited spectral ranges have been studied [8,9] [10] [11] [12] using the effective Hamiltonian approach. Despite many efforts, a simulation of the room-temperature SF₆ absorbance using effective spectroscopic models was not sufficiently complete. For this reason, the most advanced spectroscopic databases (as HITRAN [13] or GEISA [14]) do not contain line parameters for all necessary SF₆ bands in order to describe the absorbance at room temperature with high accuracy.

An approach based on *ab initio* potential energy surfaces (PES) and dipole moment surfaces (DMS) using variational methods for the solution of the full-dimensional nuclear motion Schrödinger equation, has been successfully applied to many 4-5 atomic [15] [16] [17] [18] [19] [20] [21] [22] [7], and also to six-atomic [23] [24] [25] molecules like C₂H₄. In [26] some calculated levels of UF₆ molecule having the same octahedral symmetry have been reported. However, high precision full-dimensional PESs and DMSs for seven-atomic molecules are still lacking in the literature.

Several works used alternative methods for the nuclear motion calculations for medium and large molecules using vibrational configuration-interaction approach or the perturbation theory ([27] [28] [29] and references herein). However in most cases the rotation states were computed for low J only and the contribution of hot bands have been neglected.

To compute energy levels and IR spectra beyond the harmonic oscillator approximation using *ab initio* techniques, it is necessary to obtain either the PES on a sufficiently large grid of nuclear displacements or the force field with high order derivatives. Both techniques are often used, but for high-resolution applications the technique based on an analytical PES determined at an extended geometrical grid has proved to produce more accurate results [21] [30] [26]. In the full-grid approach, the computational difficulties are related to a simultaneous account of relatively large number of electrons (70 electrons in case of SF₆) and of large number of degrees of freedom including representative nuclear geometries for the PES and DMS parametrization. As a rule, a number of different geometries is several times bigger than the number of the fitted PES parameters. The force field technique often uses the finite difference method for calculating the force constants, and as a rule, a validity of the obtained force field could not be checked for sufficiently large nuclear displacements. To reduce the number of nuclear geometries in the electronic structure calculations, it is necessary to take into account the molecular symmetry.

This paper is devoted to first calculations of the full-dimensional PES and DMS of SF₆ molecule and is structured as follows. Equilibrium structure at various basis sets, the coordinate choice and analytical model for PES and DMS surfaces are considered in Section 2 whereas *ab initio* calculations and fits are discussed in Sections 3 and 4. Calculation of the vibrational-

rotation spectra using the variation techniques [31] [32] [33] [34] shows a good agreement with experimental absorption cross-sections in the range of the strongest bands of $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$ isotopologues (section 5), providing a preliminary validation of *ab initio* results.

The equilibrium geometry and analytical form of PES and DMS

The SF_6 molecule belongs to the octahedral O_h point group: at the equilibrium geometry, the molecule is a cube with the S atom at the cube center, and six F atoms at centers of each edge (Fig. 1). Thus, only one geometrical parameter (S-F distance) determines this equilibrium structure unambiguously. Experimental and theoretical studies of the SF_6 equilibrium geometry have been considered in [35,36]. In order to calculate the equilibrium S-F distance, we applied coupled cluster CCSD(T) method and several versions of the correlation consistent basis sets - from valence triple-zeta (VTZ) and augmented valence triple-zeta (AVTZ) to core-valence quadruple-zeta (CVQZ) with Douglas-Kroll (DK) relativistic corrections. All *ab initio* calculation were carried out using MOLPRO suite of programs as implemented in the 2019.1 version [37] [38]. More details concerning *ab initio* methods will be given in Section 3. A comparison of results obtained for various basis sets with some empirical values is collected in Table 1.

Table 1. Energies and the equilibrium lengths of the S – F bound obtained with the optimization CCSD(T) technique using various basis sets.

Method / basis set	Energy, Hartree	Equilibrium length S – F, Å
CCSD(T) / VTZ	-996.07574167	1.57015425
CCSD(T) / CVTZ	-996.79947177	1.56003654
CCSD(T) / AVTZ	-996.14253699	1.57357635
CCSD(T) / CVTZ – DK	-998.23964874	1.56042314
CCSD(T) / VQZ	-996.30894816	1.56375885
CCSD(T) / CVQZ	-997.10132168	1.55654004
CCSD(T) / CVQZ-DK	-998.70581919	1.55702740
Empirical variational *		1.556
Ref. [39]		1.5647
Empirical value [40]		1.5622

**Preliminary result of empirical optimization of S-F distance using variational calculations of rotation energies [32] [7]*

Two calculations with two basis sets CVQZ and CVQZ-DK give values closed to the empirical ones. In any case without additional corrections it is impossible to calculate the equilibrium geometry with a precision better than 0.001 Å°.

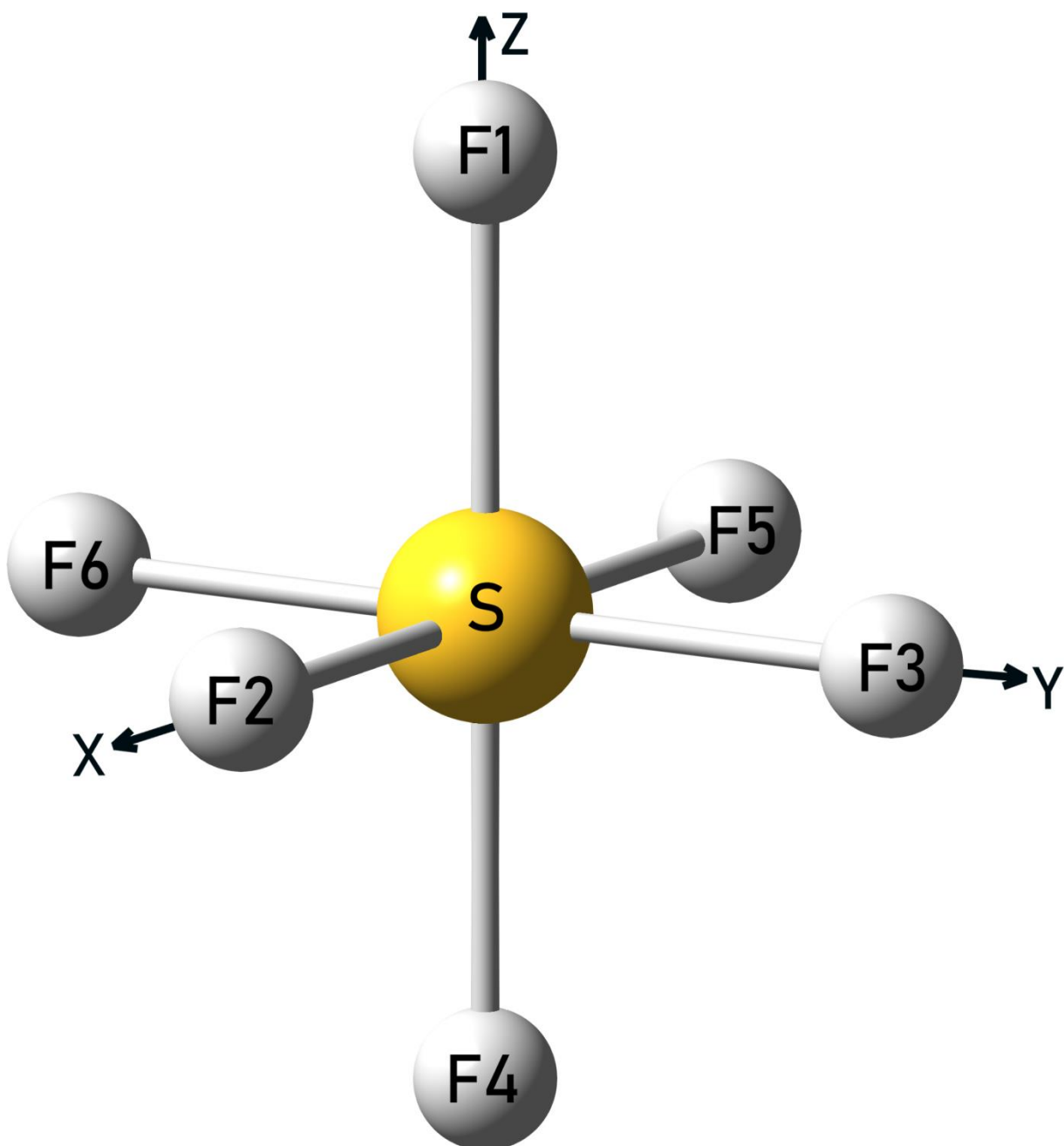


Figure 1. Equilibrium structure and the axes choice for the SF₆ molecule

Various sets of the symmetry coordinates have been used in many previous works. Most of them are incompatible with our definitions of Clebsch-Gordan coefficients for the O_h group [41] [42]. Here we use the symmetric coordinates and the molecule orientation from the work [43]. Initially, we begin with linear combinations of bond lengths and bond angles, which will be further adapted using non-linear elementary morse-type and cosine-type functions as described in Section 3. At the first step, six “radial” (stretching) symmetrized coordinates were used to accommodate three irreducible representations: A_{1g} , E_g , and F_{1u} .

$$SR_{A_{1g}} = (r_1 + r_2 + r_3 + r_4 + r_5 + r_6 - 6r_e) / \sqrt{6} \quad (1)$$

$$SR_{E_g(a)} = (2r_1 + 2r_4 - r_2 - r_3 - r_5 - r_6) / \sqrt{12} \quad (2)$$

$$SR_{F_{1u}(x)} = (r_2 - r_5) / \sqrt{2} \quad (3)$$

Nine angular coordinates q_{ij} were symmetrized according to three irreducible representations:

F_{1u} , F_{2g} , F_{2u} .

$$SA_{F_{1u}(x)} = (q_{12} + q_{23} + q_{24} + q_{26} - q_{15} - q_{35} - q_{45} - q_{56}) / \sqrt{8} \quad (4)$$

$$SA_{F_{2g}(x)} = (q_{13} + q_{46} - q_{16} - q_{34}) / 2 \quad (5)$$

$$SA_{F_{2u}(x)} = (q_{15} + q_{23} + q_{26} + q_{45} - q_{12} - q_{24} - q_{35} - q_{56}) / \sqrt{8} \quad (6)$$

Some of these q_{ij} angles in Fig 1, which take $\pi/2$ values at the equilibrium are called ‘‘adjacent’’ angles. Another ones, which take π values at the equilibrium are called ‘‘opposition’’ angles. The number of possible angles is bigger than the number of symmetrized angular coordinates. So two types of additional symmetrized angular coordinates can be added: three coordinates S'' of symmetry A_{1g} , E_g composed of ‘‘opposition’’ angles q_{14} , q_{25} , q_{36} or three coordinates S' of the same symmetry A_{1g} , E_g from 12 ‘‘adjacent’’ angles :

$$\begin{aligned} S''_{E_a} &= (q_{25} + q_{36} - 2q_{14}) / \sqrt{6} \\ S''_{E_b} &= (q_{36} - q_{25}) / \sqrt{6} \end{aligned} \quad (7)$$

$$S''_{A_{1g}} = (q_{25} + q_{36} + q_{14} - 3q''_e) / \sqrt{3}$$

$$\begin{aligned} S'_{E_a} &= (q_{12} + q_{15} + q_{34} + q_{46} + q_{13} + q_{16} + q_{24} + q_{45} - 2q_{23} - 2q_{35} - 2q_{56} - 2q_{26}) / \sqrt{24} \\ S'_{E_b} &= (q_{12} + q_{24} + q_{15} + q_{45} - q_{13} - q_{46} - q_{34} - q_{16}) / \sqrt{8} \end{aligned} \quad (8)$$

$$S'_{A_{1g}} = (q_{12} + q_{15} + q_{34} + q_{46} + q_{13} + q_{16} + q_{24} + q_{45} + q_{23} + q_{35} + q_{56} + q_{26} - 12q'_e) / \sqrt{12}$$

Here r_e is the equilibrium values for the S-F distance, q''_e and q'_e are equilibrium values for ‘‘adjacent’’ or ‘‘opposite’’ angles. The additional angular coordinates can significantly accommodate the fit of the shape of the surface near the bottom of the potential well that will affect the energy levels and wave functions. In the case of methane, this has been shown in the Refs [21].

The complete set of coordinates and the O_h group together with the matrices of irreducible representations (irrep) were reported in Ref [43]. As explained in [43], our set of internal angular coordinates is different from that of refs [44], [45], [46]. The definition of the radial symmetrized coordinates (1-3) coincides with that of [47]. Matrix representation of group elements [43] (see Table 1 of Appendix 1 for matrices) coincides with that of ref. [48] as given in our Table 2.

Table 2. O_h : point group elements

Group element	C_{31}^+	C_{4z}^+	Inversion
Transformation matrix	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
Equivalent permutations of F atoms (1 to 6)	$\begin{pmatrix} 123456 \\ 312645 \end{pmatrix}$ or $(132)(465)$	$\begin{pmatrix} 123456 \\ 162435 \end{pmatrix}$ or (2653)	$\begin{pmatrix} 123456 \\ 456123 \end{pmatrix}$ or $(14)(25)(26)$

An account of the symmetry and the use of the irreducible tensor representation permitted obtaining an optimal non-redundant grid of nuclear geometries. One grid adapted for the analytical PES development up to the 6-th order (6412 geometries) has been constructed in the work [43] using the geometry set generation technique already applied for other symmetric molecules [49] [50]. Here we use also extended grid of 78739 geometries that unambiguously define the PES development up to 8-th order constructed by the same technique. These two grids of geometries allowed us to carry out *ab initio* electronic energy calculations for a wide range of nuclear displacements. Initially, the grids were constructed in symmetrized coordinates (1-6) but for *ab initio* calculations both grids were recalculated in internal coordinates as in ref [43]: six vectors connecting the S atom with the F atoms; six lengths of the S-F bonds $\{r_1, r_2, r_3, r_4, r_5, r_6\}$; five angles between the bonds $\{q_{12}, q_{13}, q_{14}, q_{15}, q_{16}\}$, and four torsion angles $\{t_{23}, t_{24}, t_{25}, t_{26}\}$ (see Fig. 1).

In the analytical expressions for PES it is recommended to use the symmetry coordinates that are linear combinations of the internal coordinates or of 1D elementary functions of these internal coordinates. A seven-atomic molecule has 15 vibrational degrees of freedom. The standard representation in terms of the irreducible tensor operators (ITO) [41] [42] was used to obtain analytical expressions for 15-dimensional (15D) PES and DMS developments. Three stretching vibrational modes ν_1 (non-degenerate at 774.5 cm^{-1}), ν_2 (two-fold degenerate at 643.3 cm^{-1}) and ν_3 (three-fold degenerate at 948.1 cm^{-1}) transform according to the A_{1g} , E_g and F_{1u} irreducible representations while three triply degenerate bending modes ν_4 , ν_5 , and ν_6 transform under the F_{1u} (615.0 cm^{-1}), F_{2g} (524.0 cm^{-1}) and F_{2u} (347.7 cm^{-1}) representations.

The analytic potential function is written in terms of the irreducible tensor operators:

$$V(R) = \sum_{i,p} F_{ip} R_i^p(r_1, r_2, r_3, r_4, r_5, r_6, q_{12}, q_{13}, q_{14}, q_{15}, q_{16}, t_{23}, t_{24}, t_{25}, t_{26}) \quad (9)$$

where each \mathbf{R}_i^p tensor is obtained as an appropriate product of radial SR_r and angular SA_r non-linear symmetrized coordinates:

$$\mathbf{R}_i^p = \left(\left([SR_{A_{1g}}]^{p_1} \times \left([SR_{E_g}]^{p_2} \times [SR_{F_{1u}}]^{p_3} \right)^{C_{23}} \right)^{C'} \times \left([SA_{F_{1u}}]^{p_4} \times \left([SA_{F_{2g}}]^{p_5} \times [SA_{F_{2u}}]^{p_6} \right)^{C_{56}} \right)^{C''} \right)^C. \quad (10)$$

These non-linear radial SR_I and angular SA_I non-linear symmetrized coordinates involved in our PES model (9,10) were obtained by replacing the combinations (1-6) by the morse-type and cosine-type elementary functions in a similar way as was described in our works for the methane molecule [21] [49] [51]. We have tried several choices for an optimal fit to ab initio points. The final expressions of elementary functions used in the present work are given in the next Section 3. Here p_j components of $p = \{p_1, \dots, p_6\}$ correspond to powers of these coordinates and $p = p_1 + p_2 + \dots + p_6$ is the total power of the expansion term. The lower case index i corresponds to the set of symbols C_{23} , C_{56} , C , C' , C'' in the summation (9) that run over nondegenerate (A_{1g}), doubly (E_g) and triply degenerate (F_{1u} , F_{2u} , and F_{2g}) irreducible representations (irreps) of O_h point group. The C_{23} irrep results from the coupling of the symmetrized powers of the second and the third vibrational modes, whereas C' stands for the irrep corresponding to the coupling of the latter product with the symmetrized power of the first vibrational mode. In a similar manner the irrep C_{56} corresponds to the coupling of the fifth and sixth modes coupled with the fourth mode via C'' . For the PES expansion $C'=C''$, so that only the final symmetry allowed type C of the R_i^p tensors is A_{1g} . Very similar expansion can be used for the DMS, but in this case the final symmetry type C of the R_i^p tensors is F_{1u} . Each combination of the symmetrized coordinate powers p_1, \dots, p_6 and of the coupling irreps C_{23} , C_{56} , C , C' , C'' form a “tree” [41] [52]. An ITO model for the PES or for the DMS expansion at a given total order p corresponds to the summation over various symmetry allowed trees [52] with the F_{ip} parameters fitted to *ab initio* values. If the « redundant » symmetrized coordinates of the type $S'(8)$ or $S''(7)$ are included in the PES model [43], then two more corresponding factors are added at the left-hand side of the ITO tree (10).

The ITO formalism for the PES and DMS expansions can be also applied in terms of normal mode coordinates, as described in [32] [31]. This results in a similar expression to eq.(10) where the symmetrized SR_j and angular SA_k coordinates are replaced by normal coordinates Q_t . In this work we used the normal mode ITO representation for the dipole moment modeling and for intensity calculations because the matrix elements of the corresponding operators can be computed analytically. However, a sufficiently complete transformation from nonlinear symmetrized coordinates (1-6) to rectilinear normal coordinated Q_t in case of SF_6 appears to be quite complicated. In this work, we obtained the corresponding relations $\{SR_j, SA_k\} \leftrightarrow Q_t$ numerically via the solution of the system of non-linear equations. A distribution of the

RMS deviations of the fit of 15 normal coordinates to 15 internal symmetrized coordinates is shown in Fig 2. The error of the corresponding numerical solution $Q_t = Q_t(SR_j, SA_k)$ was much smaller than the precision of the fit of the analytical form (10) to *ab initio* points and thus did not affect the accuracy of the final calculation of spectra.

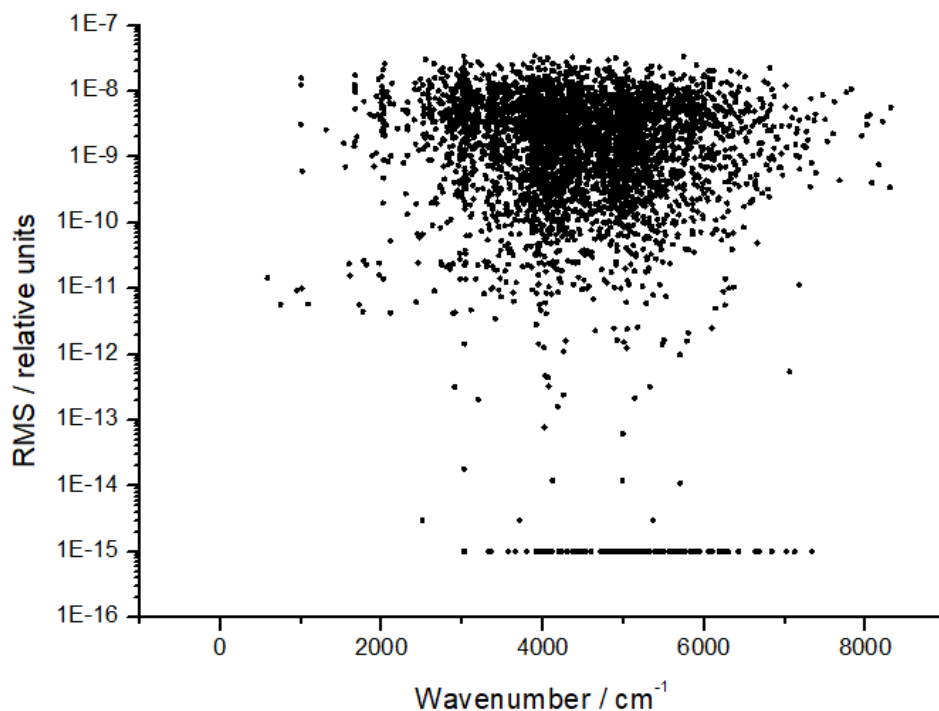


Figure 2. RMS distribution for non-linear fit of normal coordinates Q_t to internal symmetrized coordinates SR_j, SA_k

The PES calculation

To construct the molecular PES of SF_6 , we first computed a set of *ab initio* electronic energies at various molecular configurations. Equilibrium geometries and vibrational frequencies were computed with the well-established coupled cluster approach CCSD(T) with all single and double substitutions from the Hartree–Fock reference determinant augmented by a perturbative treatment of connected triple excitations [53] [54]. It was found to provide a good description for the equilibrium geometry and vibrational frequencies, and then used in this work to calculate the first full-dimensional PES of SF_6 . We used correlation consistent polarized valence n -tuple ζ -basis sets of Dunning, Peterson and co-workers [55] [56] [57] [58] for the calculations and specifically adapted Douglas-Kroll basis for calculations including relativistic effects [59]. Energies for all electronic structure calculations were converged to MOLPRO default value 10^{-10} a.u.

In order to obtain accurate calculations of vibrational and rotational energy levels from the theoretical PES useful for spectroscopic analysis, it is desirable to use high level *ab initio* methods with sufficiently large basis sets in electronic structure calculations. However, in case of SF₆, the full-grid calculations with large basis sets (like those recently employed for methane [21] [30]) are too demanding. In this work, an essential part of electronic energy calculations was performed with the CCSD(T)/VTZ ansatz at 6412 nuclear geometries of the grid optimized for the 6-th order PES. To refine the analytical PES form, the same method and the same basis set was additionally used at 2296 geometries of the 8-th order grid. In order to control the surface shape at larger nuclear displacements we carried out supplementary MP2 calculations with VTZ atomic basis on extended grid of 85136 geometries also optimized for the 8-th order PES.

Empirical PES corrections are often used to compensate the lack of accuracy of *ab initio* calculations. However, for an efficient application of an empirical optimization these corrections have to be relatively small. Typically, simple empirical corrections are used to reduce calculated minus observed deviation for the fundamental vibration frequencies, but this could produce uncontrolled errors for highly excited states if the shape of the initial *ab initio* PES is not reliably established. This is an important point for a correct modeling of “hot” bands as they could produce a significant contribution to the atmospheric absorbance by heavy molecules with relatively low vibrational modes. In case of SF₆, only a limited number of experimental vibrational frequencies is known, that can be used for a validation of *ab initio* results. *Ab initio* equilibrium geometry obtained with CVQZ and CVQZ-DK basis sets were close to empirical ones (Table 1), but calculations using CCSD(T)/ CVQZ-DK ansatz for a large grid of geometries is actually too demanding. For this reason, we have applied the algorithm of corrections similar to that of ref. [49]. First, we have computed the one-dimensional « radial » PES section using the CVQZ-DK basis set as well as electronic energies at 67 nuclear geometries sufficient to determine the force field up to the third order. Then the difference between electronic energies in 67 geometries using CVQZ-DK and VTZ basis sets was fitted to an analytical function $F_{O3}(S(r, q))$ of 15 symmetrized coordinates expanded up to 3-rd order. One dimensional radial correction functions $f_X(r)$ were constructed as a difference between two radial potentials calculated for X-basis and for VTZ basis

$$f_X(r) = V_X(r) - V_{VTZ}(r) - F_{O3}(S(r, r_e, r_e, \dots, q_e)) \quad (11)$$

where $V_X(r)$ stands for electronic energies at the radial cut and X=CVQZ-DK or VQZ. The additional one-dimensional function $F_{O3}(r, 0, 0, \dots, 0)$ was obtained from the third order correction. All other bond lengths were fixed to their equilibrium values for X and VTZ basis sets whereas all angles were fixed to their equilibrium values. Functions $f_X(r)$ for X=CVQZ-

DK is shown in Fig. 3. Note that the one-dimensional radial correction (11) near the equilibrium geometries of VTZ and X basis sets quite significantly depends on the analytical representation.

The number N of irreducible tensors of the total A_{1g} representation involved in the PES expansion (9-10) increases quite rapidly with the order. Up to the orders 2, 3, 4, 5, 6, 7, and 8 this number N is equal to 9, 31, 123, 406, 1334, 3924, and 10994, respectively. For PES parameterization, to provide the best results using the least square technique, more complex one-dimensional basis functions are used in (1-6). Morse-type functions are used as primitive radial functions

$$f_r(r_i) = 1 - \exp(-\alpha(r_i - r_e)) \quad (12)$$

involved in the definitions of the symmetrized SR_I and angular SA_I coordinates which are used to build our final analytical PES model. Although the function $f_r(r)^2$ for $\alpha = 2.0$ reproduces very accurately the one-dimensional potential of SF, but the best choice of α in (12) for full-dimensional PES was $\alpha = 1.9$. Consequently, our PES model tends to the corresponding finite asymptote at large inter-nuclear distances contrary to a simple power series expansion in $(r - r_e)$. The angular function was expressed in terms of the cosine function:

$$f_a(q_{ij}) = \cos(q_{ij}) + \alpha \cos^2(q_{ij}). \quad (13)$$

Similar to methane PES [49], it is preferable to use the value $\alpha = 1/3$ for angular functions.

The relevance of various analytical representation of the PES was checked by the quality of the PES fit on the 8-th order grid of 85136 geometries using MP2/VTZ calculated energies. Various orders of the PES expansion and various forms of the angular dependence were tested. The results of the least-squares fits using weight function $w(E)$ similar to that previously employed for methane studies [60] [49]

$$w(E) = \frac{\tanh(-0.0005(E - E_1) + 1.002002002)}{2.002002002} \quad (14)$$

where $E_1 = 7000 \text{ cm}^{-1}$, are collected in Table 3. It is seen that parameter value $\alpha = 1/3$ permitted a notable improvement of the standard deviation of the fit for 4-th and 5-th order of the PES expansion. The use of supplementary (redundant) coordinates, as reported in the case of methane [51] [21] could significantly change the PES near the equilibrium. In this work we have also evaluated a possible impact of supplementary coordinates (7), (8) for SF₆. An introduction of S' coordinate in the PES expansion has somewhat larger effect on the standard deviation than that of S'' , but in both cases the improvement of the standard deviation was smaller with respect to the inclusion of $\alpha = 1/3$ in the quadratic terms of Eq.(13). Finally, we consider that the fifth-order PES expansion provides an acceptable quality of the fit of *ab initio* energies up to 7000 cm⁻¹.

Table 3. Result of various PES fits using 85136 electronic MP2/VTZ energies.

Order	Additional angular coordinates: order, type	#Parameters	Alpha	RMS cm ⁻¹	STD cm ⁻¹
4	-	123	0.	8.29	3.71
4	O3, S'	151	0.	6.77	3.16
4	O3, S''	151	0.	8.08	3.62
4	-	123	1/3	4.58	2.13
4	O2, S'	128	1/3	3.98	1.90
4	O2, S''	128	1/3	4.27	2.05
4	O3, S'	151	1/3	3.48	1.70
4	O3, S''	151	1/3	3.89	1.91
5	-	406	0.	1.96	0.79
5	O3, S'	434	0.	1.57	0.68
5	O3, S''	434	0.	1.66	0.68
5	-	406	1/3	0.94	0.43
5	O3, S'	434	1/3	0.58	0.28
5	O3, S''	434	1/3	0.75	0.34

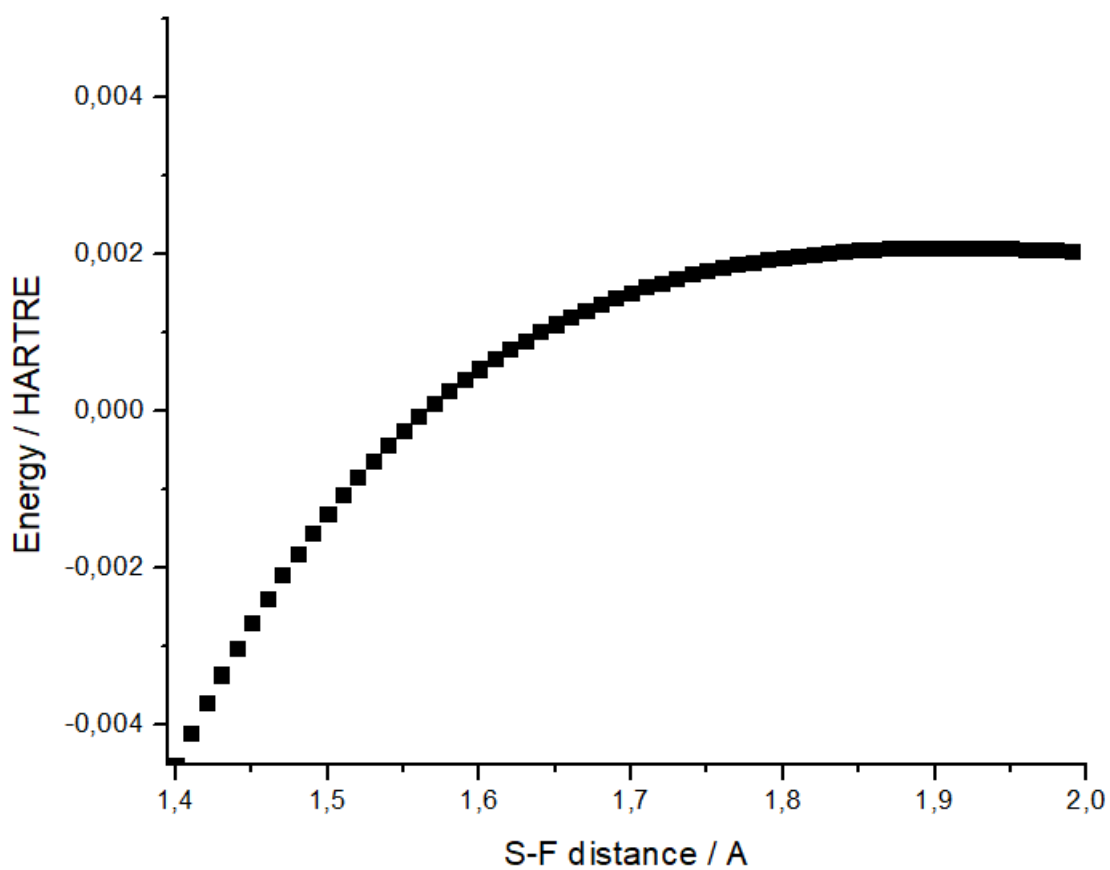


Figure 3 – One-dimensional radial correction $E\{\text{CCSD(T)-DK/CVQZ-DK}\} - E\{\text{CCSD(T)/VTZ}\}$.

The comparison of the observed fundamental band centers of $^{32}\text{SF}_6$ with our variational nuclear motion calculations using *ab initio* CCSD(T)/VTZ and CCSD(T)/CVQZ-DK surfaces is given in Table 4. For the VTZ surface defined on a large grid, vibrational and rotational energies were computed using TENSOR variational code in normal mode ITO representation. Technical detail can be found in the previous works devoted to five- and six-atomic molecules [25] [32] [33] [34]. For the VQZ surface defined on a small grid, we used an incremental scheme accounting for the relative difference $\omega_i(\text{VQZ})-\omega_i(\text{VTZ})$ between the harmonic frequencies in these basis sets as described below.

The five of six fundamentals calculated with the CVQZ-DK basis set accounting for relativistic contributions show in average better agreement with observed frequencies than VTZ calculations. Note that the most significant contribution in the increase of the fundamental frequencies of angular modes ν_4, ν_5, ν_6 when using the CVQZ-DK PES in comparison with the VTZ PES is due to the decrease of the equilibrium S-F bond length. A rough estimation of the deviations between VQZ calculations and the observed fundamental band centers (as given in column 4 of Table 4) was obtained using approximate relation $\nu_i(\text{VQZ})=\nu_i(\text{VTZ})+(\omega_i(\text{VQZ})-\omega_i(\text{VTZ}))$ where ω_i are harmonic frequencies.

Table4: The fundamental band centers (cm^{-1}) for $^{32}\text{SF}_6$: comparison of purely ab initio calculations using the VTZ and CVQZ-DK PESs with experimental values.

	Obs	Calc PES VTZ $r_e=1.57015$	Obs-Calc VTZ	Obs-Calc PES VQZ* $r_e=1.57015$	Calc PES CVQZ-DK $r_e=1.5613$	Obs-Calc CVQZ-DK
ν_1	774.5445	780.814	5.842	13.717	773.178	1.365
ν_2	643.3736	662.137	-12.113	-1.070	646.928	-3.5546
ν_3	947.9763	982.123	-25.218	-5.373	958.800	-10.824
ν_4	614.9819	613.344	5.353	11.756	620.836	-5.854
ν_5	523.449	519.258	8.766	12.495	525.897	-2.448
ν_6	347.985	347.329	3.606	7.479	351.724	-3.739

*These VQZ values in the fourth column were obtained from full dimensional variational nuclear motion calculation at the VTZ level corrected by the difference $\omega_i(\text{VQZ})-\omega_i(\text{VTZ})$ between the harmonic frequencies. The values of r_e are given in Å.

The S-F bound length computed in CVQZ-DK basis set approached towards the empirical value. This could simplify in future an empirical optimization of the PES parameters. But in order to improve the RMS deviation of the 15-dimensional PES fit with a rather small number of

parameters, the slightly increased value $r_e=1.5613$ (instead of 1.557 for CVQZ-DK) was used. The final *ab initio* PES of this work was constructed using the least-squares fit of the F_p parameters of the 5-th order expansion (9) to CCSD(T)/VTZ electronic energies at 8708 geometrical nuclear configurations with the CCSD(T)/CVQZ-DK correction as described above. In order to improve the fit accuracy near the bottom of the PES the weighting function (13) with the parameter $E_I=5000\text{ cm}^{-1}$ was applied. This permitted obtaining RMS deviation of 0.5 cm^{-1} for 4283 geometries in the range of 5000 cm^{-1} above the potential minimum. Since the order of the PES was not very high (in comparison with best methane calculations [21]), the MP2/VTZ electronic energies were not explicitly included in the fit, but were used to check the PES behavior for larger nuclear displacements.

***Ab initio* DMS fit**

Several studies [8-12] have been devoted to line-by-line analyses of experimental Raman and infrared SF₆ spectra using effective Hamiltonian and effective transition moments models. An accurate determination of empirical line intensities of heavy molecules with low frequency modes is an extremely difficult task because of crowded spectra and blended lines. One of the most challenging issue is a separation of contributions of overlapping cold and hot bands with a significant impact on the uncertainty in the temperature dependence of the absorption or emission of radiation.

Advanced *ab initio* calculations of molecular PESs and DMS together with the development of variational methods for nuclear motion calculations ([61] [62] [63] [64] [65] [18] [66] and references therein) permitted constructing quite complete lines lists for triatomic [61], [67], [68] [69] [70], four-atomic [17] [31] [71] [72] [73], five-atomic [34] [74] [30] [19] [22] [75] and six-atomic [23] [24] [25] [76] molecules. In some of these cases the accuracy of *ab initio* line intensities were competitive [77] [78] [79] [80] with best empirical determinations being more complete and reliable for the hot bands [68] [81] [82] [7] [83] [73]. On the other hand, knowledge of the shape of *ab initio* surfaces [84] [85] helped understanding issues related to molecular dynamics.

One more atom in a molecule produces three supplementary degrees of freedom in the nuclear motion resulting to a very substantial computational effort for *ab initio* predictions of high-resolution spectra for polyatomic molecules. In a brute-force approach (without symmetry considerations) there would be roughly a factor $\sim N^6$ of dimensionality between global spectra calculations of five-atomic molecule (like methane) and seven-atomic molecule like SF₆ where N is a number of *ab initio* grid points or of basis set function for each degree of freedom.

Here we present the first results for the full 15-dimensional SF₆ DMS components and for intensity calculations in the range of the strongest bands. A full account of symmetry permitted drastically reducing the number of redundant geometries and the number of independent DMS parameters. For the construction of the DMS we used the corresponding irreducible tensor representation similar to the analytical expansions (9-10) where the symmetrized internal coordinates were replaced by normal mode coordinates. The corresponding procedure has been described in our previous works [86] [71] devoted to four-atomic and five-atomic molecules. In these works, the *ab initio* DMSs were first built in molecular-fixed frames corresponding to the axes choice options of the MOLPRO code. Then the axes were rotated to the Eckart system. As in case of SF₆ the relations between internal and normal coordinated Q_i were found via numerical transformation, it was easier to proceed by direct DMS fits in normal coordinates.

A progress in methane *ab initio* calculations has taken a couple of decades [87] [60] [88] [81] [21]. The line intensity accuracy in infra-red of 1% to 5% has been recently reported [80] using the Coupled-Cluster method with ACV5Z one-particle basis sets. In case of SF₆ such calculations are presently too demanding. In this work we used CCSD(T) method with two basis sets for the dipole moment calculations. The calculations using VTZ basis were conducted on the first grid containing 1664 nuclear geometries, which was a sub-set of the 6-th order grid relative to PES computations described above. This was then supplemented by AVTZ calculations at 500 geometries. In both cases the optimal samples of geometries near the bottom of the PES were determined. At each geometry, three projections of the dipole moment were obtained. Dipole moments were computed as the derivative of the energy with respect to the weak external uniform electric field using the finite difference scheme with the field variation of 0.0002 a.u. around at the zero field strength.

For the DMS construction we used here the scheme, which has been employed in our previous works for PES and DMS of four-to-six atomic molecules [71] [86] [22] [24]. After having computed the dipole moments with AVTZ and VTZ basis sets we fitted the corresponding 15-dimensional function $diff_{2_03}(Q_i)$, which describes the corresponding difference DMS(AVTZ) - DMS(VTZ). This function was modeled by the third-order ITO expansion containing 61 adjustable parameters, of which 50 parameters were statistically well-defined. Then, for supplementary geometries from $N=501$ to $N=1664$ where the AVTZ calculations were lacking, the AVTZ dipole moments were evaluated as VTZ dipole moments plus $diff_{2_03}(Q_i)$. Finally, the fourth-order parameters of the DMS power series expansion in normal coordinates were fitted to the above defined *ab initio* dipole moment values using weight function (14) with $E_I=10000$ cm⁻¹. Of 260 fourth-order DMS parameters 194 ones were statistically well-determined. This procedure conducted to high accuracy of the fit corresponding

to the RMS deviation of $1.4\text{E-}5$ a.u. and the weighted standard deviation of $9.9\cdot 10^{-6}$. The distribution of the fit discrepancies is shown in Fig. 4.

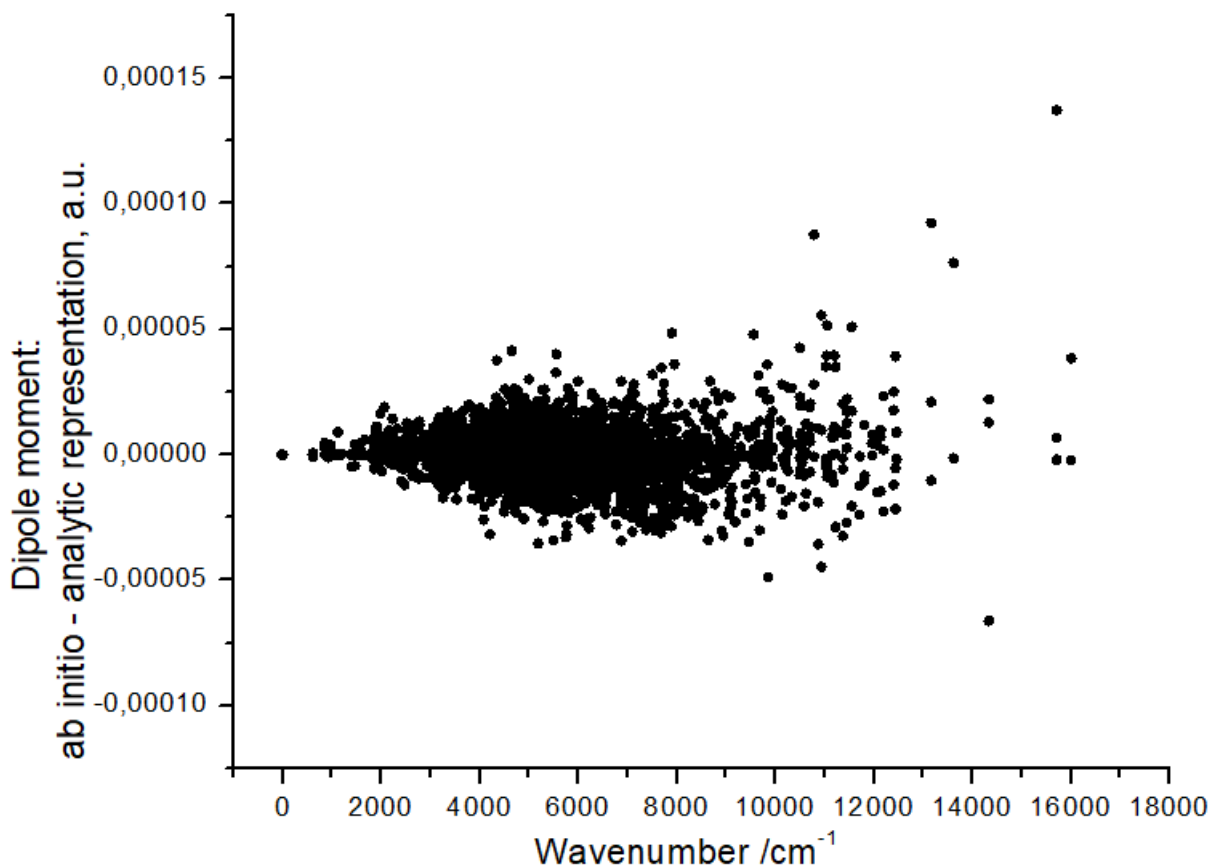


Figure 4 – Deviations between fitted analytical representation of the DMS and *ab initio* dipole moment values versus energies at the corresponding nuclear geometries.

Results and Conclusion

Preliminary evaluation of SF₆ band intensities using algorithms of variational method described in [31] [32] [33] [34] permits to conclude that our PES and DMS provided realistic predictions of absorption spectra, at least in the range of strong bands. The comparison of our calculated absorption cross-sections with experimental SF₆ cross section [89] [13] shows a very good agreement at cold temperature of 180 K, see Fig. 5, lower panel. Note that calculated band centers of ³²SF₆ and ³⁴SF₆ isotopologues in Fig. 5 were shifted to empirical values (964.196 cm⁻¹ and 932.534 cm⁻¹ correspondingly) available at <http://vamdc.icb.cnrs.fr/PHP/SF6.php>. An agreement of our calculations with experimental absorption cross-sections of Sharp et al [90] at room temperature is also satisfactory (Fig. 5, upper panel). The latter ones have been recorded at

T=298 K with N₂ pressure of 760 Torr with medium resolution of 0.112 cm⁻¹ and included in HITRAN-on-line cross-section compilation [90] [13] [91]. The absorption feature near 930 cm⁻¹ corresponds to the ν_3 band of the ³⁴SF₆ isotopologue at natural abundance. Our *ab initio* cross-sections agree much better with these observations than the simulations using SF₆ line-by-line lists constructed from effective models as available in HITRAN_2016 [13] , GEISA_2015 [14] and Dijon (SheCaSDa) [92] databases as shown in Fig. 5, upper panel. However, *ab initio* room-temperature simulations appear to be slightly less accurate than for 180 K (Fig. 5, lower panel).

Calculations at room temperature require an account of more significant contributions of hot bands involving higher vibrational states. The preliminary data obtained in this work will be made available through the TheoReTS [66] (<http://theorets.univ-reims.fr>, <http://theorets.tsu.ru>) information system. A further improvement could be possibly obtained using larger vibrational basis set that is computationally very demanding. We plan to extend the computation of full line lists in future studies.

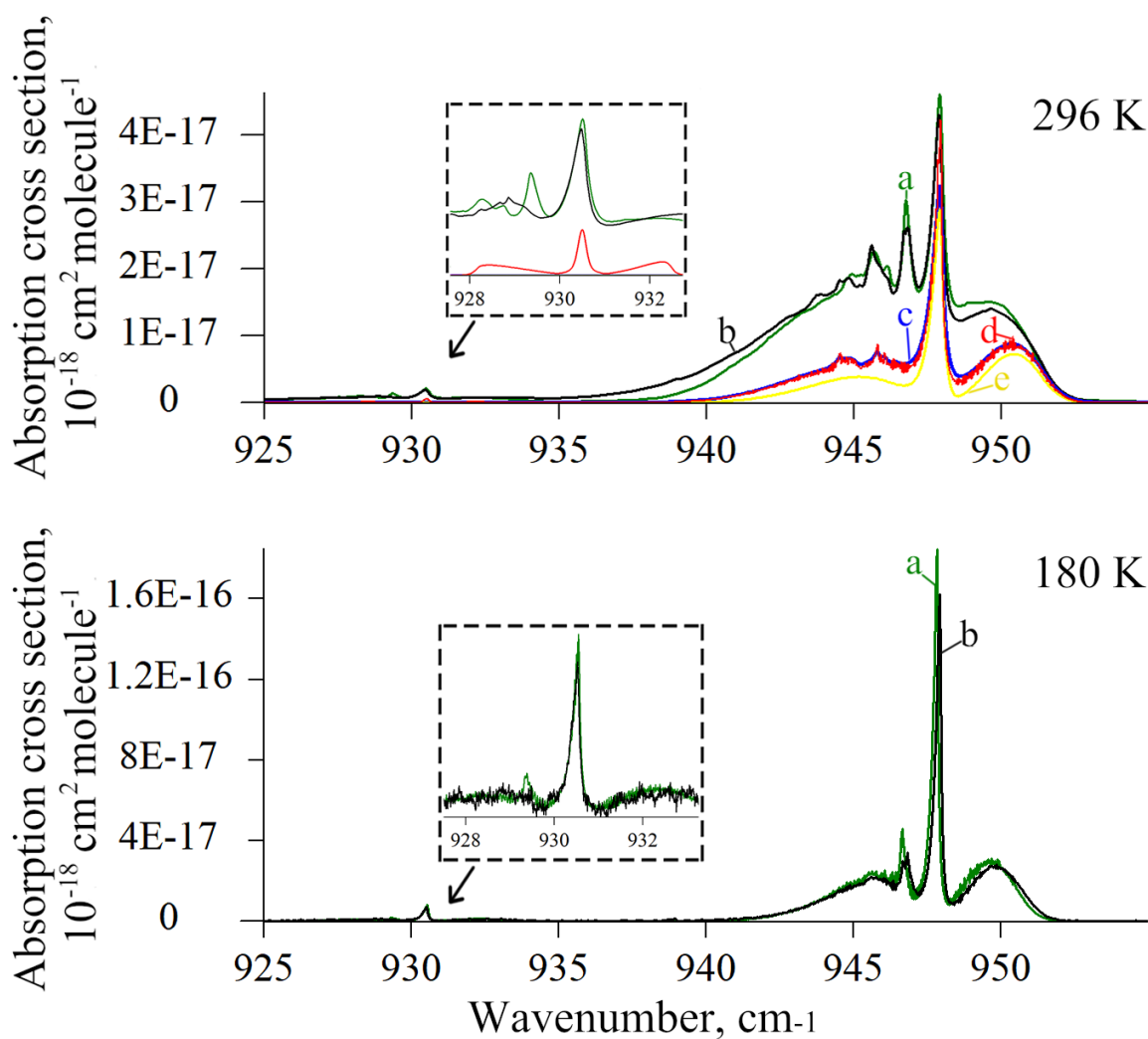


Figure 5. Comparison of cross section at a temperature of 296K (Upper panel) and of 180K (Lower panel). Upper panel: our simulation from line list of TheoReTS (green - a), the experimentally observed PNNL spectrum available in HITRAN (black -b), simulation from line list of GEISA 2015 (blue -c), the theoretical calculation of Dijon (red - d) and simulation from line list of HITRAN 2016 database (yellow - e). Lower panel: our simulation from line list of TheoReTS (green - a), the experimental observed spectrum from HITRAN (black -b)

Acknowledgements

The research in IOA was performed as part of the state assignment of the IOA SB RAS. V.T. acknowledges the support from Academic D..Mendeleev program of Tomsk State University and M.R. form LEFE CHAT CNRS program.

Supplementary Materials

In the Supplementary Materials, we provide PES in the internal coordinates and DMS in normal mode expansion in an easy to use explicit form for $^{32}\text{SF}_6$

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TOC Graphic

