Anharmonic force field and vibrational frequencies of tetrafluoromethane (CF\textsubscript{4}) and tetrafluorosilane (SiF\textsubscript{4})

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Accurate quartic anharmonic force fields for CF\textsubscript{4} and SiF\textsubscript{4} have been calculated using the CCSD(T) method and basis sets of spd f quality. Based on the \textit{ab initio} force field with a minor empirical adjustment, the vibrational energy levels of these two molecules and their isotopomers are calculated by means of high order Canonical Van Vleck Perturbation Theory (CVPT) based on curvilinear coordinates. The calculated energies agree very well with the experimental data. The full quadratic force field of CF\textsubscript{4} is further refined to the experimental data. The symmetrization of the Cartesian basis for any combination bands of \textit{T}\textsubscript{d} group molecules is discussed using the circular promotion operator for the doubly degenerate modes, together with tabulated vector coupling coefficients. The extraction of the spectroscopic constants from our second order transformed Hamiltonian in curvilinear coordinates is discussed, and compared to a similar procedure in rectilinear coordinates.

I. INTRODUCTION

Carbon tetrafluoride (also know as Freon-14) and tetrafluorosilane are molecules of wide ranging industrial, environmental, and economical interest. While the use of carbon tetrafluoride is being phased out together with that of other CFCs, it has a number of other important industrial and technological applications. These include use as an isolator and extinguisher gas in high-voltage applications, and as an etching gas in the semiconductor industry. The formation of CF\textsubscript{4}...O\textsubscript{2} adducts was considered as a model system for the use of liquid perfluorochemicals in artificial blood. Tetrafluorosilane, SiF\textsubscript{4}, is a precursor (e.g. by glow discharge in SiF\textsubscript{4}-H\textsubscript{2} mixtures) of amorphous Si-F-H semiconductors as well as for plasma deposition of low-dielectric Si-O-F thin solid films. It is the main by-product of beam etching of both semiconductors with fluorine, and silicon dioxide with fluorocarbons. In addition to being used to monitor the above processes [see e.g. Ref. [3]], SiF\textsubscript{4} has been proposed as a remote volcano monitoring probe, since its presence can be measured using open-path FT-IR spectroscopy of \nu\textsubscript{1}(SiF\textsubscript{4}). Finally, the isotopic separation of \textsuperscript{30}Si (in \textsuperscript{30}SiF\textsubscript{4}) by infrared multi-photon dissociation (IRMPD) of natural-abundance Si\textsubscript{2}F\textsubscript{6} using CO\textsubscript{2} lasers has been reported on a preparative scale.

A key step for elucidating these processes is to understand the equilibrium structure, spectroscopy and energetics of these molecules. For these reasons the vibrational spectroscopy of the above molecules has been the subject of several theoretical and experimental studies. It is also the subject of the present paper in which we apply a combination of an accurate \textit{ab initio} electronic structure treatment and a high-order CVPT treatment of the vibrational problem to the CF\textsubscript{4} and SiF\textsubscript{4} molecules.

Early gas-phase spectroscopic measurements of the CF\textsubscript{4} molecule have been reviewed and supplemented by Jones, Kennedy, and Ekberg (JKE). Earlier, Jeannotte \textit{et al.} obtained spectra in liquid argon solution, which as expected differ considerably from the JKE results due to solvent shifts. Early high-resolution work on the molecule was stimulated by the announcement of mid-infrared CF\textsubscript{4} lasing based on the \nu\textsubscript{2} + \nu\textsubscript{4} \rightarrow \nu\textsubscript{2} transition. Escherick \textit{et al.} determined \nu\textsubscript{1} to high resolution by inverse Raman spectroscopy. High-resolution
Raman spectroscopy of $\nu_2$ was carried out by Lolck and of $2\nu_2$ and $\nu_1$ by Tabyaoui et al. The $\nu_2 + \nu_4$ combination band was measured to high accuracy by Patterson et al. and by Poussigue et al. The $\nu_1$ band was studied extensively by Jones et al. by Tarrago et al. and by McDowell et al., the latter of whom determined $\nu_4$ for all three isotopic species with Doppler-limited resolution. Doppler-limited measurements of the $2\nu_1 + \nu_4$ combination band were published by two different groups. A Fermi type 1 interaction exists between $2\nu_4$ and $\nu_3$, detailed analyses of the $\nu_3$ and $2\nu_3$ and of the $\nu_3/2\nu_4$ polyad have been carried out.

The spectroscopic studies of CF$_4$ have been accompanied by several theoretical (spectroscopic) investigations. Harmonic valence force fields were first derived by Duncan and Mills and by Chalmers and McKeen. Jeannotte et al. fitted a harmonic potential, supplemented by diagonal cubic and quartic stretching force constants only, to their earlier liquid argon solution measurements. Brodersen obtained a cubic force field from experimental rotation-vibration data. A quartic force field is said to be partly refined to rovibrational levels below 1400 cm$^{-1}$, but detailed information about the fitting is unavailable so far. At higher energies, Boujut et al. consider local and normal mode behavior in the $\nu_3$ and $\nu_4$ ladders of tetrahedral XY$_4$ and octahedral XY$_6$ molecules, with CF$_4$ being considered among the former. In their analysis they employ data from Ref. 24 as computerized into the STDS data bank. The $n\nu_3$ ladder has also been found to be a good testing ground for comparing experiment and theory. Using their results of high-resolution proton energy loss spectroscopy, Maring et al. review earlier data for $\nu_3$, $2\nu_3$, and $3\nu_3$. They also summarize earlier unpublished data by Heenan who derived two sets of Hecht type anharmonic constants (to be denoted Heenan I and Heenan II in the remainder of the paper) from fitting Urey-Bradley type force fields to the Jeannotte and JKE data, respectively. Maring et al. propose some alterations based on their measurements, including an apparently exceptionally large value for $X_{13} = -9.1$ cm$^{-1}$.

Early work on the spectroscopy of SiF$_4$ has been reviewed by McDowell et al. who note that research on the molecule was stimulated by the fact that the $\nu_3$ fundamental overlaps the $P$ branch of the 9400 nm band of the CO$_2$ laser. McDowell and coworkers reported a partial set of anharmonic force constants as well. In recent theoretical work, the low lying vibrational spectrum of SiF$_4$ has been modeled using an algebraic approach.

Patterson and Pink determined $B_0 = 0.13676(3)$ cm$^{-1}$, whence $r_0 = 1.55982(17)$ Å. In later work, Takami and Kuzu and later Jörissen et al. substantially revised $B_0$ upward (to 0.137780439(92) cm$^{-1}$, consistent with a substantially shorter $r_0 = 1.55404$ Å). As this paper was being finalized, we received a preprint by Demaison et al., in which $r_e = 1.5524(8)$ is derived from a combination of ab initio and experimental results.

In the present paper we re-investigate the spectroscopy of these molecules using a combination of accurate ab initio anharmonic force fields and advanced techniques for solving the vibrational Schrödinger equation. In an earlier electronic structure study, Martin and Taylor revisited the heat of vaporization of silicon (which, among other things, is required for any ab initio or semiempirical calculation of the heat of formation of any silicon compound) from a benchmark ab initio calculation on SiF$_4$ from a very precise fluorine bomb calorimetric measurement of the heat of formation of SiF$_4(g)$ and a benchmark ab initio calculation of the total atomization energy of said molecule. In this paper, the focus is restricted to the molecular vibrations. In part, we were motivated to study these molecules due to the success of a recent study in which, an ab initio quartic force field for methane obtained using large basis sets and coupled cluster methods served as the starting point for several spectral refinement studies using variational methods and high-order canonical Van Vleck perturbation theory. In general, we find that only the quadratic force constants and perhaps the geometry needs to be refined, and most of the remainder of the force field can be constrained to the ab initio values.

II. AB INITIO ANHARMONIC FORCE FIELD

All electronic structure calculations were carried out using MOLPRO 97 running on an SGI Origin 2000 minisupercomputer at the Weizmann Institute of Science.

Electronic correlation was treated at the CCSD(T) level [coupled cluster with all single and double substitutions (CCSD) supplemented with a quasiperturbative estimate of the contribution of connected triple excitations (CCSDT) method, using the implementation thereof in MOLPRO]. This method is known to yield correlation energies that are very close to the exact basis set correlation energy (i.e. the full configuration interaction result in the same basis set) as long as correlation is predominantly dynamical in character. As pointed out previously, correlation in SiF$_4$ is essentially purely dynamical in character, and the same holds true for CF$_4$. For the record, values for the $T_1$ diagnostic (a measure for the importance of nondynamical
correlation) are only 0.0118 for SiF$_4$ and 0.0119 for CF$_4$, respectively. (In all calculations reported here, only valence electrons were correlated.)

Geometry optimizations were carried out by univariate polynomial interpolation. At the reference geometry, a quartic force field in curvilinear symmetry coordinates was determined by recursive application of the central finite difference formula with step size 0.01 Å or radian. (Quartic contamination was removed from the quadratic force constants.) The symmetry coordinates are the same as those used in the previous study on CH$_4$.

The resulting curvilinear internal coordinate force field was then transformed to rectilinear normal coordinates, then a standard second-order rovibrational perturbation theory was carried out by means of the SPECTRO program. The alignment conventions for the anharmonic constants of a spherical top follow the work of Hecht and general formulae for these constants were taken from the paper by Hodgkinson et al. (See Section III.B for a discussion about the definition of the $\nu_2$ normal coordinates.) The implementation in SPECTRO was slightly modified to allow deperturbing for an arbitrary number of Fermi resonances and a simple routine implementing Hecht's energy level formulas up to four vibrational quanta was added. Similar procedure has also been implemented in the curvilinear formalism, and the relationship between the two formalism will be discussed in Section III.B. As in past work (e.g. Ref. 45), correct alignment was verified by slightly (0.00001 a.m.u.) perturbing the masses of two atoms, then repeating the analysis in the asymmetric top formalism.

Given the $n^3N^4$ scaling (with $n$ the number of electrons correlated and $N$ the number of basis functions) of CPU time for a CCSD(T) calculation, the large number of valence electrons correlated ($n=32$) imposes certain restrictions on the size of the basis set for a complete quartic force field. We settled on the standard Dunning cc-pVTZ (correlation consistent polarized valence triple zeta) basis set (150 contracted Gaussian-type functions, CGTFs) for CF$_4$, while for SiF$_4$, we opted for the cc-pVTZ+1 basis set (159 CGTFs), where the suffix ”+1” denotes the addition of a single high-exponent $d$ function on second-row elements to accommodate inner polarization effects. The latter has been repeatedly shown to be essential for accurate computed properties of second-row molecules with polar bonds, and the addition of a mere five functions to the basis set increases CPU time insignificantly for our purposes. It should be pointed out that even with these relatively compact basis sets, the evaluation of each force field took the equivalent of six weeks of CPU time on the SGI Origin.

For purposes of validation, we in addition calculated geometries and harmonic frequencies at the CCSD(T) level with a number of other basis sets. For CF$_4$, we considered the (diffuse-function) augmented cc-pVTZ basis set aug-cc-pVTZ of Kendall et al. (230 CGTFs), while for SiF$_4$, we considered both the standard cc-pVTZ basis set (154 CGTFs) and the aug-cc-pVTZ+1 basis set (239 CGTFs), in which the ”+1” suffix again denotes the addition of an inner-polarization $d$ function. The results are collected in Tables I and II.

For CF$_4$, the main deficiency appears to be that the asymmetric stretching frequency $\omega_3$ is seriously overestimated. This is a known problem for polar bonds, particularly those involving fluorine — and given the $N^4$ scaling behavior would increase CPU time requirements by one and two orders of magnitude, respectively, and would therefore be essentially impossible. The use of anion basis set (i.e. aug-cc-pV$n$Z) on at least the electronegative atoms themselves generally leads to a dramatic improvement in basis set convergence and here too we see that CCSD(T)/aug-cc-pVTZ frequencies for CF$_4$ are much closer to the final adjusted values than the CCSD(T)/cc-pVTZ values. While in HF, this sensitivity extends to the anharmonicities in heavy-atom systems like FNO and ClNO, the anharmonicities are generally unaffected by this change. We have therefore chosen not to calculate the entire anharmonic force field at the CCSD(T)/aug-cc-pVTZ level, which would have increased CPU time requirements approximately fivefold.

Interestingly, the effect of adding the anion functions is much less pronounced for SiF$_4$ than it is for CF$_4$. The effect of adding the inner polarization function is fairly pronounced on the bond distance (a decrease of almost 0.01 Å), but effects on the harmonic frequencies are fairly minor. Here too, we judged that the CCSD(T)/cc-pVTZ+1 level represented the best compromise between accuracy and computational cost for the entire anharmonic force field.

Purely ab initio calculation of the geometry and the harmonic part of the potential would presumably be feasible as far as basis set convergence and inner-shell correlation corrections are concerned, but we know from experience that imperfections in the CCSD(T) method might still account for (usually positive) errors of several cm$^{-1}$ in the frequencies. Full configuration interaction calculations are out of the question for this system, and hence we have followed a different track similar to previous work on silane and refined the ‘raw’ CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVTZ+1 force fields in the following way.

(1) Using standard second-order rovibrational perturbation theory, the four vibrational fundamentals for the most abundant isotopomer were obtained, together with the equilibrium and ground-state rotational
constants $B_e$ and $B_0$, respectively. Hence (as $r_e \sqrt{B_e/B_0}$) the computed $r_0$ was obtained.

(2) Using the internal coordinate force field given above, the four diagonal quadratic force constants and $r_e$ were then iteratively adjusted such that the fundamentals and $r_0$ obtained by second-order rovibrational perturbation theory coincide with the experimental values to the precision given. ($F_{47}$ and all cubic and quartic force constants were held at their \textit{ab initio} computed values.) This process converged after three iterations, and the final force fields are given in Table III. This force field was then used as input for the higher-order vibrational analysis.

As can be seen in Tables IV and V, the adjustment only entails relatively minor changes in the geometry and harmonic frequencies. In addition, overall agreement between the available experimental energy levels and the values computed using standard second-order perturbation theory is such that we conclude that the CCSD(T)/VTZ(+1) quartic force fields are of sufficient quality for our purposes. (Since the computed energy levels are essentially identical to those obtained by means of second-order CVPT if no resonances are accounted for, the reader is referred to Tables VI and VII and the relevant sections below for details.)

Concerning the equilibrium geometries, we note that our final $r_e$ values for CF$_4$ and SiF$_4$ agree with the experimentally derived values of Brodersen \textit{et al.} and Demaison \textit{et al.}, respectively, to within their stated uncertainties.

III. CALCULATION OF VIBRATION ENERGY LEVELS

In this and the following two sections, in order to assess the accuracy of the \textit{ab initio} force field, the vibrational energy levels of CF$_4$ and SiF$_4$ are calculated using high order canonical Van Vleck perturbation theory (CVPT) and compared to the experimental data. The calculation is similar to that which has been recently applied to the methane and its isotopomers. Details about this calculation can be found in Ref. \textit{48}, and only the major procedures will be summarized here.

Firstly the exact $J = 0$ vibrational Hamiltonian including the pseudo-potential $V'$ term is expanded in terms of the curvilinear normal coordinates based on the Morse coordinates for the stretch and angle extension coordinates for the bend. The redundancy relation between the six bond angles is properly taken into account in the expansion. As in the case of methane and its isotopomers, the kinetic energy operators are expanded to fourth order, even though CVPT is carried out to a higher order. We choose this scheme because the kinetic contributions of order higher than four are believed to be small, and the number of terms rapidly increases with the order of the expansion. The quartic potential which is already in expanded form is used throughout this work. It contributes to the CVPT up to the second order. It is re-expressed in the coordinates described above so that the new expansion of the potential agrees with the original potential up to quartic terms.

The expanded Hamiltonian is separated in the form

$$H_v = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \cdots + \lambda^n H^{(n)},$$

where $\lambda$ is the perturbation parameter. A succession of canonical transformations of the form

$$K_v = \exp\{i\lambda^n[S^{(n)}, ]\} \cdots \exp\{i\lambda^2[S^{(2)}, ]\} \exp\{i\lambda[S^{(1)}, ]\}H_v$$

are then applied to the Hamiltonian of Eq. (1), where the $S^{(n)}$ are chosen such that the matrix representation of $K_v$ is block diagonal through order $n$. The blocks are characterized by one or more polyad quantum numbers

$$N_l = \sum_i m_i v_i,$$

where the integers $m_i$ define the block. These integers are chosen such that the resonance interactions are not perturbatively decoupled. Details regarding the choice of the polyad quantum numbers will be discussed later with respect to specific molecules.

Two points, regarding our analysis of this Hamiltonian are now considered in more detail. First, in order to obtain and analyze the eigenvalues of the individual blocks we diagonalize each block in a \textit{symmetrized basis} to reduce the matrix size and to help assign the calculated levels. Second, the transformed (effective) Hamiltonian of Eq. (2) at second order is particularly interesting as its coefficients are the quartic anharmonicity constants and resonance constants, which have been conventionally used by spectroscopists to highlight the features of the vibrational spectra. In the following two subsections we discuss the basis symmetrization and extraction of spectroscopic constants as they have not been given in our previous work.
A. Symmetrization in the Cartesian basis for the \( T_d \) point group

There are generally two ways of choosing basis functions for the doubly and triply degenerated normal modes for the \( T_d \) group molecules. The first choice (angular momentum basis) are eigenfunctions of the vibrational angular momenta. The second choice (Cartesian basis) is the products of harmonic oscillator functions including different Cartesian components of the degenerate vibrations. In the angular momentum basis, the off-diagonal terms are the spherical tensor operators defined by Hecht\cite{76} and their matrix elements are calculated using the Wigner-Eckart theorem. However it is more difficult to treat vibrational resonances in the angular momentum basis, and therefore the alternative Cartesian basis is more often used. Another advantage of the Cartesian basis is that the matrix elements are readily calculated since they all reduce to one-dimensional harmonic oscillator matrix elements. For both basis, the symmetrization is nonobvious and we are going to discuss the symmetrization in the Cartesian basis below.

The Cartesian basis denoted by \( |n_1; n_2, n_3, n_4; n_{a}, n_{b}, n_{c} \rangle \) will be symmetrized into the irreducible representations of the \( T_d \) point group: \( A_d, A, E, F_1 \) and \( F_2 \). Various equivalent approaches can be used, such as the projection operator technique\cite{77} and the promotion operator technique with tabulated vector coupling coefficients.\cite{77} The vector coupling coefficients (also called Clebsch-Gordan coefficients) \( \langle \Gamma_1 \Gamma_2 \Gamma_c \rangle \) defined in

\[
\langle \Gamma_1 \Gamma_2 \Gamma_c \rangle = \sum_{a,b} \langle \Gamma_1 \Gamma_2 ab \rangle \langle \Gamma_1 \Gamma_2 ab \rangle \langle \Gamma_1 \Gamma_2 \Gamma_c \rangle \tag{4}
\]

and tabulated in Table A20 of Ref. \cite{76} (See also Table 1 of Ref. \cite{77}) essentially determine how the product basis from two basis \( |\Gamma_1 a \rangle \) and \( |\Gamma_2 b \rangle \) are further reduced according to the irreducible representation \( |\Gamma_c \rangle \) of the point group. In this work, the latter method is adopted with some improvements to attain unique symmetrization.

First of all, the overtone of the \( E (\nu_2) \) and \( F_2 (\nu_3 \text{ and } \nu_4) \) normal modes are symmetrized separately. For the symmetrization of the overtone of the \( E \) normal modes, the promotion operators technique with tabulated vector coupling coefficients has been used in Ref. \cite{77}. The method is summarized as follows. The promotion operators with \( (E_a, E_b) \) symmetry are the familiar creation operators which act on the basis by

\[
\begin{align*}
\hat{a}_a^\dagger (E_a) & |n_a, n_b\rangle = \sqrt{n_a + 1} |n_a + 1, n_b\rangle \\
\hat{a}_b^\dagger (E_b) & |n_a, n_b\rangle = \sqrt{n_b + 1} |n_a, n_b + 1\rangle.
\end{align*}
\tag{5}
\]

Taking the promotion operators to belong to \( (E_a, E_b) \) symmetries, the symmetry of the resultant promoted basis function can be identified according to the vector coupling coefficients. Starting from the \( \nu=1 \) basis function, one can derive all the symmetrized basis functions until \( \nu \) reaches a given number similar to climbing a \( \nu \) ladder. A computer code is desirable if one wants to symmetrize a high overtone. One problem is that spurious states with the same symmetry may arise if the promotion operator acts on every basis, and they are not orthogonal. For example, with promotion operators acting on the full \( 3\nu_2 \) symmetrized basis \( (A_1 + A_2 + E) \), three nonorthogonal \( E \) states are obtained while only two are allowed for \( 4\nu_2 \). These spurious states are removed by using the Gram-Schmidt orthogonalization technique. The final orthogonal symmetrized basis is not unique, but all possible solutions lead to symmetrized Hamiltonian matrix blocks.

An alternative method, which yields unique symmetrization coefficients, is obtained by finding the exact decomposition of the angular momentum basis function into the Cartesian basis wavefunction. Once this is done, the symmetrization is trivial as the angular momentum basis function is readily symmetrized according to the value \( l \) modulo 3. This task seems quite complicated since the angular momentum basis functions are basically the associated Laguerre polynomials and the Cartesian basis functions are essentially products of two Hermite polynomials. In fact, this complication can be circumvented by using the circular promotion operators defined by

\[
\begin{align*}
\hat{a}_a^\dagger & = \frac{1}{\sqrt{2}} (a_a^\dagger + ia_b^\dagger) \\
\hat{a}_b^\dagger & = \frac{1}{\sqrt{2}} (a_a^\dagger - ia_b^\dagger)
\end{align*}
\tag{6}
\]

They act on the angular momentum basis by

\[
a^\dagger_j |\nu\rangle = \sqrt{\frac{(\nu + l)}{2} + 1} (\nu + 1)^l |
u\rangle
\]

5
Following a convention which is learned from Eq. (9), the \( D \) transform the angular momentum basis functions to the real cosine and sine form, which are members of $\{ | l \rangle \}$. The key difference is that the basis functions symmetrized there are products of ten functions based on the ten $A$ and on the Cartesian basis by

\[
\begin{align*}
\alpha_a^+|v\rangle &= \frac{\sqrt{n_a + 1}}{2}|n_a + 1, n_b\rangle + i\frac{\sqrt{n_b + 1}}{2}|n_a, n_b + 1\rangle \\
\alpha_d^+|n_a, n_b\rangle &= \frac{\sqrt{n_a + 1}}{2}|n_a + 1, n_b\rangle + i\frac{\sqrt{n_b + 1}}{2}|n_a, n_b + 1\rangle \\
\alpha_g^+|n_a, n_b\rangle &= \frac{\sqrt{n_a + 1}}{2}|n_a + 1, n_b\rangle - i\frac{\sqrt{n_b + 1}}{2}|n_a, n_b + 1\rangle
\end{align*}
\]

With the circular promotion operators acting on the $v = 0$ ground state $|0\rangle = |0, 0\rangle$ in the two basis sets, respectively, one obtains the relationship for the $v = 1$ basis

\[
|1\rangle = \frac{\sqrt{2}}{2}(|10\rangle \pm i|01\rangle)
\]

Repeating this operation up to a given quantum number $v$ leads to relationship of the two basis up to $v$. The next step is to transform the angular momentum basis from the $(E^\pm, E^-)$ to $(E_a, E_b)$ symmetries. It is well known that $|v^{\pm l}\rangle$ ($l = 3p + 1$, with $p$ being any integer) form a basis for $E^\pm$ irreducible representations. Following a convention which is learned from Eq. (8), the $(E_a, E_b)$ symmetry basis functions are defined by

\[
\begin{align*}
|v|^{E_a}\rangle &= \frac{\sqrt{2}}{2}(|v^{+}\rangle + |v^{-}\rangle) = \sqrt{2} \text{Re}(|v^{+}\rangle) \\
|v|^{E_b}\rangle &= \frac{\sqrt{2}}{2i}(|v^{+}\rangle - |v^{-}\rangle) = \sqrt{2} \text{Im}(|v^{+}\rangle)
\end{align*}
\]

where $l = 3p + 1$. The $A_1/A_2$ symmetry basis functions are defined similarly by

\[
\begin{align*}
|v|^{A_1}\rangle &= \frac{\sqrt{2}}{2}(|v^{+}|\rangle + |v^{-}|\rangle) = \sqrt{2} \text{Re}(|v^{+}|\rangle) \\
|v|^{A_2}\rangle &= \frac{\sqrt{2}}{2i}(|v^{+}|\rangle - |v^{-}|\rangle) = \sqrt{2} \text{Im}(|v^{+}|\rangle)
\end{align*}
\]

where $l = 3p$. There is only $A_1$ symmetry if $l$ is zero. Pak et al.\cite{ref8} have also discussed a similar scheme to transform the angular momentum basis functions to the real cosine and sine form, which are members of the irreducible representation of the $D_{3h}$ group. It should be noted that the above results can be applied to other analogous doubly degenerated modes such as the $E$ mode in the $C_{3v}$ group and the $E_g$ mode in the $O_h$ group. The above procedure can be easily implemented by a computer code. Results up to $v = 8$ are listed in Table 4, which are obtained from a code in the Maple computer algebra language. These results may be useful for other applications. A Fortran code is also written for the same purpose and is to be combined with the symmetrization of the $F_2$ normal mode to form a general symmetrization package.

Now we turn to the symmetrization of the overtone of the $F_2$ normal mode. This can also be achieved using the promotion operators together with the vector coupling coefficients. However there exist general rules on how a given overtone is symmetrized without resorting to promotion of lower states. These general rules can be derived using the projection operator methods. Roughly speaking, one obtains $AE$ symmetry when the three Cartesian quantum numbers are all even or odd, and $F$ symmetry when they are mixed even and odd. Detailed symmetrization coefficients have been given in Table 2 of Ref. 30 for the overtone of the triply degenerated modes ($F_1$ and $F_2$ modes of $T_d$ group) of $O_h$ and $T_d$ group.

Finally, given the fact that the $E$ overtone and $F_2$ overtone have been symmetrized separately, the combination bands in the form $(n_1n_2n_3n_4)$ can be symmetrized using the vector coupling coefficients, as has been demonstrated in Ref. 22. In this process, no spurious states arise as the basis functions joining the product are from different normal modes. All the above steps have been implemented as a Fortran code which writes to a file the symmetrization coefficients for all the combination bands in a polyad with a given polyad number. This is highly desirable since one may encounter completely different polyad numbers such as those for CH$_4$, CF$_4$ and SiF$_4$. These symmetrization coefficients are further used in constructing the polyad block matrix of the transformed Hamiltonian.

It is interesting to compare with the basis symmetrization for the $T_d$ group in the algebraic mode. A key difference is that the basis functions symmetrized there are products of ten functions based on the ten
internal coordinates. Due to the redundancy between the six bond-angle coordinates considerable effort was required to remove the so-called spurious states. Their symmetrization procedure is basically the same as the promotion operator technique with tabulated vector coupling coefficients.

Lemus and Frank have also tabulated and derived part of the vector coupling coefficients in the $T_d$ group, unaware of an earlier full tabulation.

B. Extraction of spectroscopic constants

The spectroscopic constants we want to extract from our second order transformed Hamiltonian are specifically the quartic anharmonicity constants $X_{ij}$, $G_{ij}$, the tensor constants $T_{ij}$ and $S_{ij}$ and the cubic $K_{i,jk}$ and quartic resonance constants $K_{i,jkl}$ and $K_{ij,kl}$. The quartic anharmonicity constants $X_{ij}$ and $G_{ij}$ have their usual definitions. The tensor constants were defined by Hecht as coefficients of spherical tensor operators which cause splittings of the same symmetry components of the overtone and combination bands of spherical top molecules. This procedure has been used in earlier work on the acetylene molecule, however the procedure used was not described. More importantly, the procedure has not been applied to molecules of $T_d$ symmetry which present a special challenge. For these reasons we describe the procedure in full detail here.

The apparent difficulty of the extraction is that our CVPT results for the transformed Hamiltonian are expressed as expansions of creation-annihilation operators in normal form — the creation operators are put before the annihilation operators. These expansion terms need to be rearranged to obtain the traditional spectroscopic Hamiltonian. A simple example based on second order perturbation theory serves to illustrate this point. At second order the normal form expansion includes contributions, such as \( \hat{a}_1^\dagger \hat{a}_1^\dagger \hat{a}_1 \), where \( \hat{a}_1 \) is a creation operator and \( \hat{a}_1^\dagger \) its corresponding annihilation operator. The expansion terms need to be rearranged to obtain the traditional spectroscopic form where only quadratic terms such as \( \hat{a}_1^\dagger \hat{a}_1 + \frac{1}{2} \) contribute. With either choice of expansion the leading term will have the same coefficient which is $X_{11}$.

A similar problem has been studied by Hodgkinson et al. who have suggested the same idea of extracting spectroscopic constants from the second order transformed Hamiltonian, although the Hamiltonian discussed there is in rectilinear normal coordinates and the creation-annihilation operators are not rearranged to normal form. Furthermore, the extraction of constants related with doubly and triply degenerated modes requires one more step than the above simple example of $X_{11}$. For example, the tensor constants $T_{23}$ and anharmonicity constants $X_{23}$ are determined simultaneously by

\[
\text{Coeff}(\hat{n}_{2a}\hat{n}_{2z}) = X_{23} + 8T_{23} \\
\text{Coeff}(\hat{n}_{2b}\hat{n}_{2z}) = X_{23} - 8T_{23}
\]

Equation (12) is a pertinent example. Finally, it is noted that the vector coupling coefficients tabulated by Tababe and Sugano and Griffith agree with Mills’ definition of the symmetry coordinates of $\nu_2$.

The extraction of the resonance constants is straightforward in the creation-annihilation form since they are usually defined in this form. One just needs to take care of constructing the correctly symmetrized Hamiltonian terms for the resonance. To this end, several equivalent approaches can be used. Other than the method by Hecht for constructing the correctly symmetrized potential tensor operators, we choose...
to follow an elegant and more general approach by Halonen who used the tabulated vector coupling coefficients to construct the correctly symmetrized Hamiltonian terms from any combination of operators such as coordinates, momenta and creation-annihilation operators. Methane has a variety of cubic and quartic resonances due to its approximate 2:1 ratio of the stretch and bend frequency. Halonen has given for the first time all the correctly symmetrized Darling-Dennison type quartic resonance terms in Ref. 75 using the vector coupling methods. The resonance constants encountered in CF₄ and SiF₄ are limited compared to methane. Up to second order resonance, they are (See also Eqs. (13) – (14) and (23) – (25))

\[
H/hc = K_{1,22} \left[ a_1^\dagger (a_{2a}^2 + a_{2b}^2) + h.c. \right]
\]

(13)

\[
H/hc = K_{3,44} \left[ a_1^\dagger a_{3a} a_{4y} a_{4z} + a_1^\dagger a_{3y} a_{4x} + a_1^\dagger a_{3z} a_{4x} a_{4y} + h.c. \right]
\]

(14)

for CF₄ and

\[
H/hc = K_{1,44} \left[ a_1^\dagger (a_{4x}^2 + a_{4y}^2 + a_{4z}^2) \right] + h.c.
\]

(15)

\[
H/hc = K_{1,222} \left[ a_1^\dagger a_{2a} (a_{2a}^2 - 3a_{2b}^2) \right] + h.c.
\]

(16)

for SiF₄. The quartic resonance with coefficient \(K_{1,222}\) is of a new type. We shall show how it is derived to illustrate the vector coupling method. The goal is to construct the totally symmetric (\(A_1\) symmetry) quartic terms from one creation operator (\(a_1^\dagger\)) with \(A_1\) symmetry and two annihilation operators (\(a_{2a}, a_{2b}\)) with \(E\) symmetry. Apparently there is only one such term. First the \(E_a/E_b\) symmetry quadratic terms are constructed from products of (\(a_{2a}, a_{2b}\)) and themselves as follows

\[
E_a : \frac{1}{\sqrt{2}} (-a_{2a}^2 + a_{2b}^2)
\]

\[
E_b : \sqrt{2} a_{2a} a_{2b}
\]

(17)

Then the \(A_1\) symmetry cubic terms are constructed from products of (\(a_{2a}, a_{2b}\)) and the two terms of Eq. (17) as follows

\[
A_1 : \frac{1}{\sqrt{2}} \left[ \frac{1}{\sqrt{2}} (-a_{2a}^2 + a_{2b}^2) \cdot a_{2a} + \sqrt{2} a_{2a} a_{2b} \cdot a_{2b} \right]
\]

\[
= -\frac{1}{2} a_{2a} (a_{2a}^2 - 3a_{2b}^2)
\]

(18)

Finally the \(A_1\) symmetry quartic term is obtained as product of \(a_1^\dagger\) and terms of Eq. (18) plus the Hermite conjugate of the product. The coefficient of the final resonance term in Eq. (18) has been redefined for convenience.

An interesting point is that the anharmonicity and tensor constants extracted using the method above agree exactly with standard second-order perturbation theory in rectilinear normal coordinates as implemented in SPECTRO, provided that the same force field is used and no resonances are considered. This seems to be a surprise, since the reported CVPT results are based on curvilinear coordinates. McCoy and Sibert have explained this as follows. When using dimensionless normal coordinates the perturbation parameter in the expansion of Eq. (1) can be taken as \(\hbar^{1/2}\). Here terms of order \(n\) in Eq. (1) are of order \(\hbar^{(2+n)/2}\). This is true regardless of using rectilinear or curvilinear normal coordinates. Since both sets have identical zero-order Hamiltonians, the energies have to be identical order by order. If one uses perturbation theory to transform to block-diagonal Hamiltonian, which is subsequently diagonalized, the above argument breaks down, and notable differences have been found. In this work, a multi-resonance Hamiltonian has been considered for CF₄ and SiF₄. Therefore the spectroscopic constants are extracted from the second order CVPT transformed Hamiltonian, and some of them are different from those obtained using SPECTRO with resonances deperturbed. More details regarding this point are given with respect to CF₄ and SiF₄ molecules in the following section.

**IV. RESULTS FOR CF₄**

The choice of the polyad quantum numbers for CF₄ is based on the following considerations. The harmonic frequencies as calculated from the \(ab\) \textit{initio} force fields (\(\omega_1 = 921.57\) cm\(^{-1}\), \(\omega_2 = 439.91\) cm\(^{-1}\), \(\omega_3 = 1303.01\) cm\(^{-1}\), \(\omega_4 = 637.89\) cm\(^{-1}\)) suggest that three independent resonances are possible:
\[ \omega_1 \approx 2\omega_2 \]  \hspace{1cm} (19)  
\[ \omega_3 \approx 2\omega_4 \]  \hspace{1cm} (20)  
\[ 3\omega_2 \approx \omega_3 \]  \hspace{1cm} (21)  

The frequency differences between the above pairs are only 42 cm\(^{-1}\), 27 cm\(^{-1}\) and 17 cm\(^{-1}\), respectively. Since these small differences will go into the denominator of the expression of \(S^{(n)}\), they will possibly lead to divergence of the perturbation theory when the coupling strength between the two pair states are not negligible. In practice we found that all the three resonances should be as strong as the (0020; F) band should be as strong as the (0012) and (0004) bands, although the major perturbant (0012) is a little farther away.

Fermi interactions illustrate the points made in the previous section. The corresponding constants in the rectilinear formalism, where different, are given in footnotes. The refined constants are given in Table V and the comparison of experimental and calculated energy levels is given in Table VI. The RMSD (root mean squares deviations) based on the refined potential is 0.179, 0.083 and 0.083 cm\(^{-1}\) at second, fourth and sixth order CVPT, respectively, whereas the corresponding RMSD based on the ab initio potential in Table IV is 0.095, 0.190 and 0.186 cm\(^{-1}\). This shows that the ab initio potential is a rather good as an initial potential for the fitting. The following remarks can be made by examining the calculated results in Table V.

1. The CVPT calculation converges very well. The energy level changes typically on the order of 0.1 cm\(^{-1}\) by comparing the fourth and sixth order results. This contrasts with the case of CH\(_4\) where the bending overtone (4\(v_4\)) varies by about three wavenumbers at the eighth order. Therefore the fourth order CVPT is used for the fitting. The contribution due to the \(V^2\) terms is small. For example, the largest contribution to the fundamentals is 0.057 cm\(^{-1}\) for (0001; F\(_2\)) band of \(^{12}\)CF\(_4\) using sixth order CVPT.

2. For \(^{12}\)CF\(_4\), the resonance \(\omega_3 \approx 2\omega_4\) is the most pronounced. Even the (0010; F\(_2\)) fundamental has 7\% admixture from (0002; F\(_2\)). The resonance \(\omega_1 \approx 2\omega_2\) is less pronounced and the resonance \(3\omega_2 \approx \omega_3\) can be ignored. The above remarks also apply for the \(^{14}\)CF\(_4\) whereas all the three resonances seem to be less pronounced for \(^{14}\)CF\(_4\).

3. The calculations for the three (0020) bands using either the ab initio or fitted force field cannot reproduce well the observations which were obtained through a rovibrational analysis of the isolated (0020) bands. We cannot fully understand these discrepancies. But it is clear that the (0020) band in Fermi resonance with the (0012) and (0004) bands, although the major perturbant (0012) is a little farther away. For example, the three (0012; F\(_2\)) bands are respectively at 2536.50 cm\(^{-1}\), 2541.66 cm\(^{-1}\), and 2544.45 cm\(^{-1}\). We have also noted that near the experimental (0020; F\(_2\)) band origins (2561.91 cm\(^{-1}\)), there is a band calculated to be 2561.04 cm\(^{-1}\) with 82\%(0302; F\(_2\)) and 14\%(0310; F\(_2\)). However it is very unlikely that this band should be as strong as the (0020; F\(_2\)) band. Further theoretical and experimental work on this band system appears to be desirable.

Finally, the vibrational spectroscopic constants for all the isotopes of CF\(_4\) and SiF\(_4\) obtained from the second order transformed CVPT Hamiltonian (curvilinear formalism) are given in Table VII. With these constants one can reproduce the second order CVPT calculation by constructing the block diagonal Hamiltonian matrices. The corresponding constants in the rectilinear formalism, where different, are given in footnotes to said table. The differences (for the Fermi resonance constants and for such anharmonic constants as are affected by the Fermi interactions) illustrate the points made in the previous section.

Discrepancies between the presently computed anharmonicity constants and the empirically derived sets of Heenan mostly reflect the limitations of the latter in terms of available data. There is no indication

\[ N = 4v_1 + 2v_2 + 6v_3 + 3v_4, \]  \hspace{1cm} (22)
for the very high $X_{33} = -9.1 \text{ cm}^{-1}$ as suggested by Maring et al.\textsuperscript{32} We also note that both Heenan sets of harmonic frequencies differ quite substantially from our best values, and are confident that the latter are more reliable.

V. RESULTS FOR SiF$_4$

The choice of the polyad quantum numbers for SiF$_4$ is based on the following considerations. The harmonic frequencies as calculated from the \textit{ab initio} force fields ($\omega_1 = 806.3 \text{ cm}^{-1}$, $\omega_2 = 265.2 \text{ cm}^{-1}$, $\omega_3 = 1044.0 \text{ cm}^{-1}$, $\omega_4 = 389.3 \text{ cm}^{-1}$) suggest that three independent resonances are possible:

\begin{align}
\omega_1 &\approx 2\omega_4 \\
\omega_1 + \omega_2 &\approx \omega_3 \\
\omega_1 &\approx 3\omega_2
\end{align}

The differences between the above pairs are only 27 cm$^{-1}$, 27 cm$^{-1}$, and 11 cm$^{-1}$, respectively. Again all three resonances ought to be considered to ensure good convergence when the perturbation theory is carried up to sixth order. It should be noted that the resonance in Eq. (24) is actually a third order resonance, because the symmetry is unmatched between $\nu_1 + \nu_2$ ($F_2$) and $\nu_3$ ($E$) at first order. Following the approach of the previous section the good quantum number, to be used in the perturbative calculations, is found to be

\begin{equation}
N = 6v_1 + 2v_2 + 8v_3 + 3v_4
\end{equation}

which we are going to use in the perturbation calculations reported below.

The sixteen observed band centers from Ref.\textsuperscript{35} and the values of the second, fourth and sixth order CVPT calculations are given in Table \textbf{VIII}. The following remarks can be made by examining Table \textbf{VIII}.

(1) The calculated values converges to a few hundredths of a wavenumber by comparing the fourth and sixth order results. The convergence is better than in the case of CF$_4$. The contribution due to the $V'$ terms is small. For example, the largest contribution to the fundamentals is 0.0016 cm$^{-1}$ for (0001;F$_2$) band of $^{28}$SiF$_4$ using sixth order CVPT. This is smaller than that of the $^{12}$CF$_4$ since SiF$_4$ is heavier.

(2) The agreement between calculation and experiment is rather good with a RMSD of 0.59, 0.74 and 0.73 cm$^{-1}$ at second, fourth and sixth order CVPT, respectively. It should be noted that the slightly better agreement at the second order is fortuitous as the second order results still do not converge. On the whole, the CVPT results are remarkable in spite of the fact that the CVPT calculation uses the \textit{ab initio} force field where only four diagonal quadratic force constants were optimized to the four experimental fundamentals. The success of the perturbation calculation is mainly due to the small anharmonicity for this relatively heavy-atom molecule (cfr. the $\omega_i - \nu_i$ values in Tables \textbf{I} and \textbf{II}).

(3) In Table \textbf{VIII} our calculations are compared with those of the $U(2)$ algebraic model.\textsuperscript{38} Although the $U(2)$ algebraic model yields a similar RMSD (0.79 cm$^{-1}$), nine parameters were employed to fit the sixteen vibrational data. A fit of similar quality is also reported by the same authors\textsuperscript{35} using a boson realization model. However, in both models the polyad number $N = v_1 + v_2 + v_3 + v_4$ is used and the Fermi resonance $\omega_1 \approx 2\omega_4$ is considered in neither.

(4) It can be seen from Table \textbf{VIII} that the resonance $\omega_1 \approx 2\omega_4$ is most prominent. The other two resonances are also considered to ensure good convergence at sixth order. To neglect these two resonances will considerably reduce the size of the matrix associated with a given value of the quantum number, so that high overtone states can be relatively easier to calculate. The lack of strong resonance in $\nu_2$ and its overtone ensures that the isolated treatment of the $\nu_3$ overtone is a good approximation.\textsuperscript{33} Patterson and Pine has done such a calculation, and find the Cartesian basis is much inferior to the angular momentum basis due to the near degeneracy of the Cartesian basis. This near degeneracy is specific to SiF$_4$ since the relation $G_{33} = 8T_{33}$ is nearly satisfied.\textsuperscript{34} However, as far as the calculation of the vibrational energy is concerned, both basis sets can be used.

The partial set of empirically derived anharmonicity constants (Table \textbf{VII}) of McDowell \textit{et al.}\textsuperscript{3} agrees fairly well with our computed values, while their derived harmonic frequencies agree to within their stated uncertainty with our own best values.
VI. CONCLUSIONS

The anharmonic vibrational spectra of the all-heavy atom spherical tops CF\textsubscript{4} and SiF\textsubscript{4} have been treated by the combination of an accurate \textit{ab initio} anharmonic force field and high-order canonical Van Vleck perturbation theory (CVPT).

The anharmonic part of the potential energy surface is evidently very well described at the CCSD(T)/cc-pVTZ level for CF\textsubscript{4}, and at the CCSD(T)/cc-pVTZ+1 level for SiF\textsubscript{4}, where the ‘+1’ notation refers to the addition of a high-exponent \(d\) function on second-row atoms. The harmonic frequencies of CF\textsubscript{4} exhibit substantial errors at the CCSD(T)/cc-pVTZ level, which disappear upon addition of diffuse functions to the basis set.

The force field is subsequently slightly refined by adjusting the equilibrium geometry and the diagonal quadratic force constants (in this case, five parameters) such that a standard second-order rovibrational perturbation theoretical treatment reproduces the experimental fundamentals and ground-state rotational constants of the molecules. The adjustments involved are fairly minor.

These force fields were then used as input for CVPT calculations up to sixth order inclusive. While agreement with experiment is fortuitously quite good at second order in CVPT, consistent convergence to 0.1 cm\textsuperscript{-1} in the energy level is only achieved at sixth order. However, the truncation error at second order is much less significant than in the case of hydride systems like CH\textsubscript{4} and SiH\textsubscript{4}.

RMS deviation (RMSD) between computed (sixth order CVPT) and observed energy levels with the adjusted \textit{ab initio} potentials is 0.19 cm\textsuperscript{-1} for CF\textsubscript{4} and 0.73 cm\textsuperscript{-1} for SiF\textsubscript{4}, the latter to some extent reflecting the lesser accuracy of the experimental data. In the case of CF\textsubscript{4}, improvement with experiment could be somewhat further improved (to RMSD=0.08 cm\textsuperscript{-1}) by re-adjusting both diagonal and off-diagonal quadratic force constants to the complete set of experimental vibrational level information. Experimentation with refinement of additional force field parameters yielded no further improvement.

For CF\textsubscript{4}, three resonances, Eqs. (23)–(25), were considered, of which only one (\(\omega_3 \approx 2\omega_4\)) is important. This shows that an isolated \(\nu_3\) overtone ladder model is inadequate. For SiF\textsubscript{4}, three resonances, Eqs. (19)–(21), were considered, of which only one (\(\omega_1 \approx 2\omega_4\)) is important.

An improved approach for symmetrizing combination bands in the Cartesian basis for the \(T_d\) group is proposed. We also demonstrate how anharmonic spectroscopic constants \(X_{ij}, G_{ij}, T_{ij}, S_{ij}\) can be extracted from the second-order CVPT transformed Hamiltonian (in curvilinear internal coordinates) for \(T_d\) molecules. In the absence of resonances, the results are identical to those obtained by standard second-order perturbation theory in rectilinear normal coordinates. Differences occur when the constants are being deperturbed for Fermi resonances. Accurate sets of quartic spectroscopic constants for the isotomers of CF\textsubscript{4} and SiF\textsubscript{4} are obtained. Agreement with previously published empirically derived sets of anharmonicity constants is fairly good for SiF\textsubscript{4}, but less satisfactory for CF\textsubscript{4}.

In order to stimulate further research on these molecules, sixth-order CVPT energy level predictions up to polyad number \(N = 24\) for \{12,13,14\} CF\textsubscript{4} and \{28,29,30\} SiF\textsubscript{4} have been made available on the World Wide Web at the Uniform Resource Locator (URL) \url{http://theochem.weizmann.ac.il/web/papers/cf4sif4.html}. The force fields themselves are available in machine-readable form at the same URL.

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TABLE I. Computed (CCSD(T)) and observed bond distances (Å), harmonic and fundamental frequencies (cm\(^{-1}\)) for \(^{12}\)CF\(_4\)

|        | cc-pVTZ unadj. | aug-cc-pVTZ | cc-pVTZ adjusted | Expt. |
|--------|----------------|-------------|------------------|-------|
|        | \(r_e\) | \(r_0\) | \(r_s\) | \(r_e\) | \(r_0\) | \(r_s\) | \(r_e\) | \(r_0\) | \(r_s\) | \(r_e\) | \(r_0\) | \(r_s\) |
| \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) |
| 1 | 922.80 | 910.75 | 12.26 | 915.2 | 921.57 | 909.07 | 12.50 | 909.07 | 12.50 |
| 2 | 440.00 | 435.59 | 4.40 | 435.2 | 439.91 | 435.40 | 4.51 | 435.39 | 4.51 |
| 3 | 1322.25 | 1303.15 | 19.10 | 1301.3 | 1303.01 | 1283.66 | 19.35 | 1283.66 | 19.35 |
| 4 | 638.81 | 632.22 | 6.59 | 630.4 | 637.89 | 631.06 | 6.84 | 631.06 | 6.84 |

\(a\) Ref. [28].

\(b\) From \(B_0=0.19118709(32)\) cm\(^{-1}\).

TABLE II. Computed (CCSD(T)) and observed bond distances (Å), harmonic and fundamental frequencies (cm\(^{-1}\)) for \(^{28}\)SiF\(_4\)

|        | cc-pVTZ | aug-cc-pVTZ | cc-pVTZ+1 unadj. | cc-pVTZ+1 adjusted | Expt. |
|--------|---------|-------------|-------------------|--------------------|-------|
|        | \(r_e\) | \(r_e\) | \(r_0\) | \(r_s\) | \(r_e\) | \(r_0\) | \(r_s\) | \(r_e\) | \(r_0\) | \(r_s\) | \(r_e\) | \(r_0\) | \(r_s\) |
| \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) | \(\omega_i\) | \(\nu_i\) |
| 1 | 794.9 | 794.1 | 797.86 | 792.19 | 5.67 | 806.10 | 800.60 | 5.50 | 807.1(12) | 800.6 |
| 2 | 258.9 | 258.8 | 263.18 | 262.13 | 1.05 | 265.20 | 264.20 | 1.00 | 267(3) | 264.2 |
| 3 | 1036.5 | 1029.8 | 1037.49 | 1024.31 | 13.18 | 1044.04 | 1031.40 | 12.64 | 1044.2(12) | 1031.3968 |
| 4 | 384.3 | 382.7 | 387.61 | 386.67 | 0.94 | 389.31 | 388.44 | 0.87 | 389.8(9) | 388.448 |

\(a\) Ref. [42].

\(b\) From Ref. [11]. \(B_0=0.137780439(92)\) cm\(^{-1}\). In older work \(B_0=0.13676(3)\) cm\(^{-1}\) and hence \(r_0=1.55982(17)\) Å.

TABLE III. Quadratic, cubic and quartic force constants (aJ/Å\(^{m}\)"radian") for SiF\(_4\) and CF\(_4\)

|        | SiF\(_4\) | CF\(_4\) | SiF\(_4\) | CF\(_4\) | SiF\(_4\) | CF\(_4\) |
|--------|-----------|---------|-----------|---------|-----------|---------|
| \(F_{11}\) | 7.27355 | 9.30679 | 0.63194 | 1.24913 | 6.40971 | 6.13519 |
| \(F_{44}\) | -0.34328 | -1.03126 | 1.06468 | 1.83767 | -20.29450 | -32.46123 |
| \(F_{662}\) | 0.06985 | -1.99181 | -18.73201 | -23.71962 | 0.56578 | 2.57073 |
| \(F_{77}\) | -0.97378 | 3.01480 | -5.33763 | -1.11062 | -0.60404 | -2.24497 |
| \(F_{99}\) | 0.61671 | 2.05526 | -1.01287 | -2.25675 | 18.17256 | -18.94290 |
| \(F_{55}\) | -0.17620 | -0.38638 | -0.01658 | 0.04702 | 0.86987 | 1.30646 |
| \(F_{1111}\) | 50.47669 | 89.63168 | 1.26945 | 4.44699 | 48.94503 | 71.68647 |
| \(F_{777}\) | -0.80741 | -5.46450 | 1.53293 | 5.89090 | 76.478 | 2.93285 |
| \(F_{6622}\) | 1.16338 | 5.73913 | -1.08209 | -4.08511 | 1.46146 | 4.33621 |
| \(F_{6633}\) | 48.23448 | 60.63713 | 0.40465 | 1.24159 | 0.15861 | 0.26676 |
| \(F_{99}\) | -0.63502 | -1.85550 | 0.76756 | 2.44329 | 0.76815 | 3.1691 |
| \(F_{88}\) | -0.46055 | -1.86075 | -1.12641 | -3.26978 | 0.03132 | 0.14651 |
| \(F_{9922}\) | 2.11522 | 5.37994 | 0.39929 | 0.77598 | 0.43597 | 1.12997 |
| \(F_{7772}\) | 0.01923 | 0.04530 | 50.01306 | 72.17993 | 48.79060 | 59.28204 |
| \(F_{7711}\) | -0.83975 | -6.35131 | 0.39771 | 4.50345 | 1.37066 | 5.70508 |
| \(F_{8874}\) | 0.02280 | -0.04550 | -0.53371 | -1.07258 | -2.21128 | -6.91109 |
| \(F_{8874}\) | -0.14830 | -0.36797 | 4.58572 | 11.28388 | 2.18342 | 3.67611 |
TABLE IV. The relationships of the angular momentum basis $|v^l\rangle$ and the Cartesian basis $|n_x n_y\rangle$ for the overtone of the doubly degenerated modes ($v_2$). See Eqs. (1) and (2) for definition of $A_1/A_2$ and $E_a/E_b$ symmetry wavefunction.

|   | $2^0; A_1$ | $2^2; E_a$ | $2^2; E_b$ |
|---|---|---|---|
|   | $+\sqrt{[20]}\langle 20\rangle$ | $+\sqrt{[20]}\langle 02\rangle$ | $+\sqrt{[11]}\langle 11\rangle$ |
| $3^3; A_1$ | $+\sqrt{[30]}\langle 30\rangle$ | $-\sqrt{[12]}\langle 12\rangle$ | $+\sqrt{[22]}\langle 22\rangle$ |
| $3^3; A_2$ | $-\sqrt{[30]}\langle 03\rangle$ | $+\sqrt{[21]}\langle 04\rangle$ | $+\sqrt{[13]}\langle 13\rangle$ |
| $3^3; E_a$ | $+\sqrt{[30]}\langle 30\rangle$ | $+\sqrt{[12]}\langle 12\rangle$ | $-\sqrt{[22]}\langle 22\rangle$ |
| $3^3; E_b$ | $+\sqrt{[30]}\langle 03\rangle$ | $+\sqrt{[21]}\langle 04\rangle$ | $+\sqrt{[13]}\langle 13\rangle$ |
| $4^0; A_1$ | $+\sqrt{[40]}\langle 40\rangle$ | $+\sqrt{[04]}\langle 04\rangle$ | $+\sqrt{[22]}\langle 22\rangle$ |
| $4^2; E_a$ | $+\sqrt{[40]}\langle 40\rangle$ | $-\sqrt{[04]}\langle 04\rangle$ | $+\sqrt{[14]}\langle 14\rangle$ |
| $4^2; E_b$ | $-\sqrt{[31]}\langle 31\rangle$ | $-\sqrt{[13]}\langle 13\rangle$ | $+\sqrt{[14]}\langle 14\rangle$ |
| $4^4; E_a$ | $+\sqrt{[40]}\langle 40\rangle$ | $+\sqrt{[04]}\langle 04\rangle$ | $-\sqrt{[22]}\langle 22\rangle$ |
| $4^4; E_b$ | $-\sqrt{[31]}\langle 31\rangle$ | $-\sqrt{[13]}\langle 13\rangle$ | $+\sqrt{[14]}\langle 14\rangle$ |
| $5^3; A_1$ | $+\sqrt{[50]}\langle 50\rangle$ | $-\sqrt{[32]}\langle 32\rangle$ | $-\sqrt{[14]}\langle 14\rangle$ |
| $5^3; A_2$ | $-\sqrt{[50]}\langle 05\rangle$ | $+\sqrt{[23]}\langle 23\rangle$ | $+\sqrt{[14]}\langle 14\rangle$ |
| $5^3; E_a$ | $+\sqrt{[50]}\langle 50\rangle$ | $+\sqrt{[32]}\langle 32\rangle$ | $+\sqrt{[14]}\langle 14\rangle$ |
| $5^3; E_b$ | $-\sqrt{[50]}\langle 05\rangle$ | $+\sqrt{[23]}\langle 23\rangle$ | $+\sqrt{[14]}\langle 14\rangle$ |
| $6^0; A_1$ | $+\sqrt{[60]}\langle 60\rangle$ | $+\sqrt{[06]}\langle 06\rangle$ | $+\sqrt{[24]}\langle 24\rangle$ |
| $6^2; A_2$ | $+\sqrt{[60]}\langle 60\rangle$ | $-\sqrt{[06]}\langle 06\rangle$ | $+\sqrt{[24]}\langle 24\rangle$ |
| $6^2; E_a$ | $-\sqrt{[51]}\langle 51\rangle$ | $-\sqrt{[15]}\langle 15\rangle$ | $-\sqrt{[33]}\langle 33\rangle$ |
| $6^2; E_b$ | $-\sqrt{[51]}\langle 51\rangle$ | $-\sqrt{[15]}\langle 15\rangle$ | $-\sqrt{[33]}\langle 33\rangle$ |
| $7^3; A_1$ | $+\sqrt{[70]}\langle 70\rangle$ | $-\sqrt{[52]}\langle 52\rangle$ | $-\sqrt{[16]}\langle 16\rangle$ |
| $7^3; A_2$ | $+\sqrt{[70]}\langle 07\rangle$ | $+\sqrt{[25]}\langle 25\rangle$ | $+\sqrt{[61]}\langle 61\rangle$ |
| $7^3; E_a$ | $+\sqrt{[70]}\langle 70\rangle$ | $+\sqrt{[52]}\langle 52\rangle$ | $+\sqrt{[16]}\langle 16\rangle$ |
| $7^3; E_b$ | $+\sqrt{[70]}\langle 07\rangle$ | $+\sqrt{[25]}\langle 25\rangle$ | $+\sqrt{[61]}\langle 61\rangle$ |
| $7^5; E_a$ | $+\sqrt{[70]}\langle 70\rangle$ | $+\sqrt{[52]}\langle 52\rangle$ | $+\sqrt{[16]}\langle 16\rangle$ |
| $7^5; E_b$ | $+\sqrt{[70]}\langle 07\rangle$ | $+\sqrt{[25]}\langle 25\rangle$ | $+\sqrt{[61]}\langle 61\rangle$ |
| $8^3; A_1$ | $+\sqrt{[80]}\langle 80\rangle$ | $+\sqrt{[08]}\langle 08\rangle$ | $+\sqrt{[26]}\langle 26\rangle$ |
| $8^3; A_2$ | $+\sqrt{[80]}\langle 71\rangle$ | $+\sqrt{[17]}\langle 17\rangle$ | $+\sqrt{[35]}\langle 35\rangle$ |
| $8^3; E_a$ | $+\sqrt{[80]}\langle 80\rangle$ | $+\sqrt{[08]}\langle 08\rangle$ | $+\sqrt{[26]}\langle 26\rangle$ |
| $8^3; E_b$ | $+\sqrt{[80]}\langle 71\rangle$ | $+\sqrt{[17]}\langle 17\rangle$ | $+\sqrt{[35]}\langle 35\rangle$ |
| $8^5; A_1$ | $+\sqrt{[80]}\langle 80\rangle$ | $+\sqrt{[08]}\langle 08\rangle$ | $+\sqrt{[26]}\langle 26\rangle$ |
| $8^5; A_2$ | $+\sqrt{[80]}\langle 71\rangle$ | $+\sqrt{[17]}\langle 17\rangle$ | $+\sqrt{[35]}\langle 35\rangle$ |
| $8^5; E_a$ | $+\sqrt{[80]}\langle 80\rangle$ | $+\sqrt{[08]}\langle 08\rangle$ | $+\sqrt{[26]}\langle 26\rangle$ |
| $8^5; E_b$ | $+\sqrt{[80]}\langle 71\rangle$ | $+\sqrt{[17]}\langle 17\rangle$ | $+\sqrt{[35]}\langle 35\rangle$ |
TABLE V. Comparison of *ab initio*\(^a\) and fitted quadratic force constants for CF\(_4\). (Units are consistent with aJ, Å, and radian.)

| Force Constant | \(ab\ initio\) raw\(^a\) | \(ab\ initio\) adjusted\(^b\) | Fitted\(^c\) | \(\sigma\)^d |
|----------------|-----------------|-----------------|-------------|-----------|
| \(r_e\)       | 1.31919          | 1.31526          | 1.31526     |           |
| \(F_{11}\)    | 9.54112          | 9.50679          | 9.50711     | 0.0%      |
| \(F_{22}\)    | 1.25733          | 1.24913          | 1.12477     | -10.0%    |
| \(F_{33}\)    | 6.32376          | 6.13519          | 6.18043     | +0.7%     |
| \(F_{34}\)    | -1.03160         | -1.03126         | -1.04559    | -1.4%     |
| \(F_{44}\)    | 1.84886          | 1.83767          | 1.82662     | -0.6%     |

\(^a\) Unadjusted CCSD(T)/cc-pVTZ values

\(^b\) Bond distance and diagonal quadratics adjusted to reproduce experimental \(r_0\) and \(\nu_i\)

\(^c\) Bond distance held constants; all quadratic force constants refined in fit against complete experimental data set.

\(^d\) Relative deviation of the fitted force constants from the adjusted *ab initio* force constants.
| N<sup>a</sup> | Sym | Obs<sup>b</sup> | Uncertainty | Ref. | Obs−E(2) | Obs−E(4) | Obs−E(6) | v<sub>1</sub>v<sub>2</sub>v<sub>3</sub>v<sub>4</sub>(c<sup>2</sup>)<sup>d</sup> |
|---|---|---|---|---|---|---|---|---|
| **12<sup>13</sup>C<sub>2</sub>F<sub>4</sub>** | | | | | | | | |
| 2 | E | 435.399 | 1 | | .227 | .100 | .103 | 000(100%) |
| 4 | A<sub>1</sub> | 867.90588 | 1 | | .476 | .012 | .003 | 000(97%) 1000(3%) |
| 5 | F<sub>1</sub> | 1066.6977 | 1 | | .300 | .052 | .065 | 0101(100%) |
| 5 | A<sub>1</sub> | 1066.1230 | 1 | | .320 | .135 | .112 | 0101(100%) |
| 6 | E | 1261.809 | 1 | | .303 | .184 | .148 | 0002(90%) |
| 6 | F<sub>2</sub> | 1260.430 | 1 | | .186 | .173 | .188 | 0002(93%) 0010(7%) |
| 7 | F<sub>3</sub> | 1283.720 | 1 | | .361 | .005 | .0002 | 0010(93%) 0002(7%) |
| 7 | F<sub>5</sub> | 1539.3 | 10 | | .196 | .251 | .241 | 1001(97%) 0021(3%) |
| 8 | F<sub>7</sub> | 1715.8 | 10 | | .225 | .963 | .960 | 0101(90%) 0102(90%) |
| 9 | F<sub>7</sub> | 1886.9<sup>c</sup> | – | | .623 | .887 | .912 | 0003(84%) 0011(16%) |
| 9 | F<sub>7</sub> | 1913.2 | 10 | | 2.031 | 1.050 | 1.100 | 0011(84%) 0003(16%) |
| 10 | F<sub>7</sub> | 2168.5 | 10 | | .674 | .604 | .621 | 1002(89%) 1010(90%) |
| 10 | F<sub>7</sub> | 2168.1 | 10 | | .602 | .636 | .636 | 1010(86%) 1002(9%) |
| 11 | F<sub>7</sub> | 2445.59644 | 1 | | .340 | .026 | .051 | 0010(94%) 1201(5%) |
| 12 | A<sub>1</sub> | 2554.24(8588) | – | | 6.225 | 3.072 | 3.215 | 0020(50%) 0012(41%) |
| 12 | E | 2570.013 | 1 | | 1.991 | 1.652 | 1.654 | 0020(93%) 0012(7%) |
| 12 | F<sub>7</sub> | 2561.0124 | – | | .212 | .0616 | .067 | 0020(86%) 0012(13%) |
| **14<sup>12</sup>C<sub>2</sub>F<sub>4</sub>** | | | | | | | | |
| 3 | F<sub>2</sub> | 629.2968 | 1 | | .270 | .110 | .118 | 0001(100%) |
| 5 | F<sub>2</sub> | 1064.39 | 10 | | .408 | .033 | .011 | 0101(100%) |
| 6 | F<sub>2</sub> | 1241.7 | 10 | | .251 | .014 | .009 | 0010(91%) 0002(9%) |
| 6 | F<sub>2</sub> | 1259.75 | 10 | | .755 | .138 | .160 | 0002(91%) 0010(9%) |
| 7 | F<sub>2</sub> | 1537.4 | 10 | | .078 | .116 | .107 | 1001(97%) 0201(3%) |
| 8 | F<sub>2</sub> | 1674.7 | 10 | | .099 | .081 | .087 | 0101(93%) 0102(7%) |
| 9 | F<sub>2</sub> | 1807. | 100 | | 1.074 | 1.631 | 1.630 | 0011(89%) 0003(11%) |
| 9 | F<sub>2</sub> | 1888. | – | | 1.262 | .279 | .353 | 1889.37 0003(80%) 0011(11%) |
| 10 | F<sub>2</sub> | 2145. | 100 | | .698 | .518 | .530 | 1010(92%) 1002(5%) |
| 10 | F<sub>2</sub> | 2166.3 | 10 | | .017 | .232 | .200 | 0010(92%) 1010(5%) |
| 11 | F<sub>2</sub> | 2443.3 | 10 | | .512 | .011 | .048 | 2001(94%) 1201(6%) |
| 12 | F<sub>2</sub> | 2477.5 | 10 | | .3086 | .556 | .556 | 0020(71%) 0012(26%) |

| RMSE | 0.0379 | 0.083 | 0.083 |

<sup>a</sup> N = 4v<sub>1</sub> + 2v<sub>2</sub> + 6v<sub>3</sub> + 3v<sub>4</sub>. This polyad number results from three independent resonances: ω<sub>1</sub> ≈ 2ω<sub>2</sub>, 3ω<sub>2</sub> ≈ ω<sub>3</sub>, and ω<sub>3</sub> ≈ 2ω<sub>4</sub>.

<sup>b</sup> The last figure is significant unless uncertainty in parenthesis is given otherwise.

<sup>c</sup> Uncertainty used in the fit corresponds approximately to the experimental precision. The states excluded from the fit are 3v<sub>4</sub> and 2v<sub>2</sub> + v<sub>3</sub> whose multiple F<sub>2</sub> components are unresolved, and the 2v<sub>3</sub> bands of 12<sup>13</sup>C<sub>2</sub>F<sub>4</sub>, which differs from experimental results.

<sup>d</sup> The largest two components in terms of v<sub>1</sub>v<sub>2</sub>v<sub>3</sub>v<sub>4</sub> and their percentage (c<sup>2</sup>) in the basis, based on the sixth order calculation. Only the components with the percentage larger than 1% are listed.

<sup>e</sup> There are two (0003) F<sub>2</sub> states.

<sup>f</sup> There are two (0210) F<sub>2</sub> states.
TABLE VII. Computed (second order transformed CVPT Hamiltonian) and experimentally derived vibrational spectroscopic constants of SiF$_4$ and CF$_4$ (cm$^{-1}$).

| Constants | $^{12}$CF$_4$ | $^{12}$CF$_4$ | $^{14}$CF$_4$ | $^{14}$CF$_4$ | $^{28}$SiF$_4$ | $^{28}$SiF$_4$ | $^{29}$SiF$_4$ | $^{30}$SiF$_4$ |
|-----------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| $\omega_1$ | 921.596      | 910.52       | 913.25       | 912.596      | 806.101      | 807.11(12)   | 806.104      | 806.101      |
| $\omega_2$ | 439.665      | 437.15       | 435.37       | 439.665      | 265.199      | 267.3(3)     | 265.199      | 265.199      |
| $\omega_3$ | 1302.510     | 1292.96      | 1292.26      | 1262.587     | 1044.044     | 1044.2(12)   | 1034.820     | 1026.177     |
| $\omega_4$ | 637.681      | 634.35       | 635.83       | 635.548      | 389.306      | 389.8(9)     | 387.793      | 386.320      |
| $X_{11}$  | -1.109       | -0.279       | -0.275       | -1.109       | -1.109       | -0.57(5)     | -0.669       | -0.669       |
| $X_{12}$  | -0.911$^a$   | 0.589        | 0.474        | -0.911       | -0.911       | -0.6(11)     | -0.317       | -0.317       |
| $X_{13}$  | -6.253       | 4.896        | -4.954       | -5.908       | -5.668       | -3.573       | -3.8(3)      | -3.503       |
| $X_{14}$  | 0.608        | 0.712        | 0.712        | -0.928       | -1.087       | 0.109$^c$    | 0.064(7)     | 0.056        |
| $X_{22}$  | -0.544       | -0.544       | -0.543       | -2.315       | -2.264       | -0.989       | -1.5(10)     | -0.979       |
| $X_{24}$  | -0.004       | -0.283       | -0.273       | 0.003        | 0.007        | 0.506        | 0.0(5)       | 0.503        |
| $X_{33}$  | -4.157       | -5.642       | -5.503       | -3.971       | -3.173       | -2.845       | -3.005(7)    | -2.779       |
| $X_{34}$  | -3.960$^b$   | -1.407       | -1.423       | -3.756       | -3.594       | -1.386       | -0.5(4)      | -1.350       |
| $X_{44}$  | -1.299$^b$   | -0.606       | -0.604       | -1.222       | -1.114       | 0.165$^c$    | 0.22(10)     | 0.163        |

Spectroscopic constants are identical between curvilinear and rectilinear formalisms except for those affected by resonances:

$^a$ Due to $\omega_1 \approx 2\omega_2$ resonance, in rectilinear formalism: $X_{12} = -0.606$; $X_{22} = -0.416$; $G_{22} = 0.619$; and $K_{1,22} = -2.908$ cm$^{-1}$.

$^b$ Due to $\omega_3 \approx 2\omega_4$ resonance, in rectilinear formalism: $X_{34} = -3.916$; $X_{44} = -0.142$; $G_{34} = -0.550$; $G_{44} = 0.018$; $T_{34} = 0.067$; $T_{44} = 0.024$; $S_{34} = 0.161$; and $K_{3,44} = 5.051$ cm$^{-1}$.

$^c$ Due to resonance $\omega_1 \approx 2\omega_4$, in rectilinear formalism: $X_{14} = -0.231$; $X_{44} = 0.250$; $G_{44} = -0.085$; and $K_{1,44} = 2.699$ cm$^{-1}$.
TABLE VIII. Comparison of experimental, CVPT\textsuperscript{a} and \textit{U}(2) algebraic model band origins (cm\textsuperscript{-1}) for SiF\textsubscript{4}. The \textit{ab initio} force contants of Table III are used for the CVPT calculation.

| \(N\) \textsuperscript{a} | Sym | Obs\textsuperscript{b} | Obs\textsuperscript{-}E(2) | Obs\textsuperscript{-}E(4) | Obs\textsuperscript{-}E(6) | Obs\textsuperscript{-}U(2)\textsuperscript{c} | \(v_1v_2v_3v_4(c_i^2)\) \textsuperscript{d} |
|-----------------|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2               | \(E\) | 264.2(10)       | 0.00            | -0.03           | -0.03           | -0.21           | 0100(100\%)     |
| 3               | \(F_2\) | 388.448(2)      | -0.01           | -0.03           | -0.03           | -0.41           | 0001(100%)      |
| 6               | \(A_1\) | 800.6(3)        | -0.24           | -0.30           | -0.30           | 1.03            | 1000(93\%)      |
| 6               | \(F_2\) | 776.3(5)        | -0.81           | -0.84           | -0.83           | 0.97            | 0002(100\%)     |
| 8               | \(E\) | 1064.2(4)       | 0.00            | -0.06           | -0.06           | 0.01            | 1100(92\%)      |
| 9               | \(F_2\) | 1164.2(2)       | 0.48            | 0.48            | 0.51            | 0.03            | 0003(90\%)      |
| 9               | \(F_2\) | 1189.7(3)       | -0.70           | -0.83           | -0.82           | 1.07            | 1001(90\%)      |
| 10              | \(F_2\) | 1294.05(10)     | 0.25            | 0.11            | 0.11            | 0.15            | 0110(100\%)     |
| 11              | \(F_2\) | 1418.75(10)     | 0.16            | 0.08            | 0.08            | 0.22            | 0011(100\%)     |
| 14              | \(F_2\) | 1804.5(1)\textsuperscript{e} | 1.05            | 0.70            | 0.72            | -0.21           | 0012(97\%)      | 1010(2\%)     |
| 14              | \(F_2\) | 1805.34         | 1805.49         | 1805.48         | 0012(96\%)      | 1010(4\%)       |
| 14              | \(F_2\) | 1807.20         | 1807.38         | 1807.37         | 0012(100\%)     |
| 16              | \(F_2\) | 1828.17(2)      | -0.56           | -0.65           | -0.65           | 0.57            | 1010(93%)       |
| 16              | \(F_2\) | 2059.1(3)       | -0.04           | -0.17           | -0.18           | 1.09            | 0020(100\%)     |
| 20              | \(F_2\) | 2602.55(10)\textsuperscript{f} | -0.14           | -0.71           | -0.67           | -1.24           | 1012(70\%)      | 2010(12\%)   |
| 20              | \(F_2\) | 2604.97         | 2605.28         | 2605.09         | 1012(81\%)      | 0014(9\%)       |
| 20              | \(F_2\) | 2606.96         | 2607.20         | 2607.04         | 1012(86\%)      | 0014(14\%)      |
| 20              | \(F_2\) | 2623.8(1)       | -1.30           | -1.47           | -1.43           | 0.12            | 2010(83\%)      | 1012(15\%)   |
| 24              | \(F_2\) | 3068.5(1)       | -0.74           | -1.71           | -1.68           | -0.63           | 0030(100\%)     |

\textsuperscript{a} \(N = 6v_1 + 2v_2 + 8v_3 + 3v_4\). This polyad number results from three independent resonances: \(\omega_1 + \omega_2 \approx \omega_3\), \(\omega_1 \approx 2\omega_4\), and \(\omega_1 \approx 3\omega_2\).

\textsuperscript{b} The observations are from Ref. \[35\]. Standard deviations given in parentheses.

\textsuperscript{c} The \textit{U}(2) algebraic model calculations are from Ref. \[36\].

\textsuperscript{d} The largest two components in terms of \(v_1v_2v_3v_4\) and their percentage \((c_i^2)\) in the basis, based on the sixth order calculation. Only the components with the percentage larger than 1\% are listed.

\textsuperscript{e} There are three \((0012) F_2\) states.

\textsuperscript{f} There are three \((1012) F_2\) states.