



HAL
open science

Effective Hamiltonians for the Fermi resonance – Interacting states of C_{3v} molecules

Kamil Sarka, Lucie Nová Stříteská, Adina Ceausu-Velcescu

► **To cite this version:**

Kamil Sarka, Lucie Nová Stříteská, Adina Ceausu-Velcescu. Effective Hamiltonians for the Fermi resonance – Interacting states of C_{3v} molecules. *Journal of Molecular Spectroscopy*, 2014, 311, pp.84-99. 10.1016/j.jms.2014.09.003 . hal-01143140

HAL Id: hal-01143140

<https://hal.science/hal-01143140>

Submitted on 22 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effective Hamiltonians for the Fermi resonance – Interacting states of C_{3v} molecules

Kamil Sarka ^a, Lucie Nová Stříteská ^{a,b,*}, Adina Ceausu-Velcescu ^c

^a Faculty of Pharmacy, Comenius University, Odbojárov 10, 832 32 Bratislava, Slovakia

^b Department of Analytical Chemistry, Institute of Chemical Technology, Technická 5, 166 25 Prague 6, Czech Republic

^c Université de Perpignan Via Domitia, Laboratoire de Mathématiques et Physique, 52 Avenue Paul Alduy, 66860 Perpignan Cedex, France

A global reduction theory of the vibration–rotational Hamiltonian of C_{3v} closed-shell molecules, dealing with all possible anharmonic interactions in which a fundamental vibration can be involved, is presented. The effective correlation-free Hamiltonians and the corresponding matrix elements are derived. The cases studied here are (i) a fundamental band interacting with an overtone, (ii) a fundamental band interacting with a combination band. The Hamiltonian terms \mathbf{H}_{30} , \mathbf{H}_{31} , \mathbf{H}_{32} and the recommended set of parameters following from the appropriate reductions are presented. The results are provided in a form directly applicable to the analysis of spectra of the interacting states.

1. Introduction

The polyads of interacting states are usually studied by high resolution spectroscopy. The high quality data require adequate treatment by Hamiltonians including higher order terms. However the more Hamiltonian terms one uses, the higher is the danger of running into correlation problems concerning the determined parameters. The correlation problems can be partly solved by means of using a ‘reduced Hamiltonian’ set of parameters [1,2].

The concept of the ‘reduced effective Hamiltonian’ was developed by Watson [1,2] and applied to isolated non-degenerate vibrational states. For such states it is a purely rotational problem. Extension to the degenerate vibrational states and to the states with accidental resonances, which represent vibrational–rotational problems, was done by Tyuterev and coworkers [3–5]. They also treated the anharmonic resonance between the states of asymmetric rotors [5]. We have recently derived [6] the effective correlation-free Hamiltonian with the corresponding matrix elements for the problem of interacting close lying states $v_t(E)$, $v_n(A_1) + v_{t'}(E)$ of C_{3v} molecules.

The aim of this paper is to provide answers to very practical questions related to spectroscopic data fitting, such as the number of constraints to be applied, the parameters which should be

constrained, the effects of the applied constraints on the physical meaning of the remaining parameters. However, the reduction schemes are ‘state specific’, in the sense that each type of vibrational state or polyad of vibrational states requires specific reduction [7].

In the present contribution, we have studied the following cases of anharmonic resonances in C_{3v} molecules: (i) a fundamental band interacting with an overtone, (ii) a fundamental band interacting with a combination band. The fundamental band can be totally symmetric $v_n(A_1) = 1$ or doubly degenerate $v_t(E) = 1$. The overtone can be $v_n(A_1) = 2$ or $v_t(E) = 2$. The combination band can be $v_n(A_1) = 1$, $v_{n'}(A_1) = 1$ or $v_n(A_1) = 1$, $v_t(E) = 1$ or $v_t(E) = 1$, $v_{t'}(E) = 1$.

This means that the following ten cases are treated in this paper:

1. $v_n(A_1) \leftrightarrow v_{n'} + v_{n''}(A_1)$
2. $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$
3. $v_n(A_1) \leftrightarrow v_{n'} + v_t(E)$
4. $v_n(A_1) \leftrightarrow v_t + v_{t'}(A_1 + A_2 + E)$
5. $v_n(A_1) \leftrightarrow 2v_t(A_1 + E)$
6. $v_t(E) \leftrightarrow v_n + v_{t'}(E)$
7. $v_t(E) \leftrightarrow v_n + v_{n'}(A_1)$
8. $v_t(E) \leftrightarrow 2v_n(A_1)$
9. $v_t(E) \leftrightarrow v_{t'} + v_{t''}(A_1 + A_2 + E)$
10. $v_t(E) \leftrightarrow 2v_{t'}(A_1 + E)$

* Corresponding author. Address: Technická 5, 166 25 Prague, Czech Republic.
E-mail address: Lucie.Striteska@vscht.cz (L.N. Stříteská).

In the following, we are giving the Hamiltonian terms, matrix elements and sets of correlation-free Hamiltonian parameters for the above listed ten types of anharmonic resonances. The results for the case (6) were already published in a short Note [6] and are presented here just for the sake of completeness.

2. Theory

2.1. The effective Hamiltonian

The effective vibration–rotational Hamiltonian for two interacting vibrational states of a symmetric-top molecule can be written as

$$\mathbf{H} = \sum_{i,m,n} X_i^{mn} V_i(q_x, p_x)^m R_i(\mathbf{J}^2, \mathbf{J}_\pm, \mathbf{J}_z)^n = \sum_{m,n} \mathbf{H}_{mn},$$

in which the molecular parameters X_i^{mn} appear as coefficients of products of vibrational V_i and rotational R_i operators. The respective total powers m and n of the vibrational and rotational operators are conventionally used for estimation of the order of magnitude of the Hamiltonian terms and parameters.

The Hamiltonian \mathbf{H} for the problem can further be split into three components [4,8,9]

$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + \mathbf{H}_{int}, \quad (1)$$

where \mathbf{H}_1 is the rovibrational Hamiltonian for the first state (A_1 or E fundamental), \mathbf{H}_2 , the rovibrational Hamiltonian for the second state (overtone or combination), and \mathbf{H}_{int} , the rovibrational Hamiltonian for the interaction between the two vibrational states. The Hamiltonians $\mathbf{H}_1, \mathbf{H}_2$ have the standard forms. There are four types of them: Hamiltonian for nondegenerate states [3,9–11] (nondegenerate fundamental $v_n(A_1)$, nondegenerate overtone $2v_n(A_1)$, nondegenerate combination band $v_{n'} + v_{n''}(A_1)$), Hamiltonian for degenerate states [3,9–11] (degenerate fundamental $v_t(E)$, degenerate combination band $v_{t'} + v_t(E)$), Hamiltonian for degenerate overtones of the type $2v_{t'}(A_1 + E)$ [12], Hamiltonian for degenerate combination bands of the type $v_t + v_{t'}(A_1 + A_2 + E)$ [13–15]. At the level of approximation used in the present work, the diagonal terms up to \mathbf{H}_{23} and the intra-vibrational interaction terms up to \mathbf{H}_{24} have been considered. For the $v_{t'} = 2(A_1 + E)$ overtone levels or the $v_t = v_{t'} = 1(A_1 + A_2 + E)$ combination levels, we have also included the $\mathbf{H}_{4n}(n = 0, 1)$ terms [12,15].

The interaction Hamiltonians \mathbf{H}_{int} are presented in Appendix A, where we have used the ladder operators [3,4,8,10,11,16]

$$\mathcal{L}_n^\sigma = q_n - i\sigma p_n, \quad \mathbf{J}_\sigma = \mathbf{J}_x + i\sigma \mathbf{J}_y \quad (\sigma = \pm 1) \quad (2)$$

and the “double ladder” operators [8–11,17]

$$\begin{aligned} \mathcal{L}_\varepsilon^\sigma &= \frac{1}{2}[(q_a + i\varepsilon q_b) - i\sigma(p_a + i\varepsilon p_b)] \quad (\sigma, \varepsilon \\ &= \pm 1, \text{ the two signs are independent}). \end{aligned} \quad (3)$$

The laddering properties of the operators

$$\begin{aligned} \mathcal{L}_n^\sigma |v_n\rangle &= [2v_n + \sigma + 1]^{1/2} |v_n + \sigma\rangle \\ \mathbf{J}_\sigma \mathbf{J}, k &= [J(J+1) - k(k-\sigma)]^{1/2} |J, k - \sigma\rangle \\ \mathcal{L}_{t\varepsilon}^\sigma |v_t, l_t\rangle &= [(v_t + \sigma \varepsilon l_t + \sigma + 1)/2]^{1/2} |v_t + \sigma, l_t + \varepsilon\rangle \end{aligned} \quad (4)$$

provide the matrix elements presented in Appendix B.

We have considered the three lowest terms ($\mathbf{H}_{int} = \mathbf{H}_{30} + \mathbf{H}_{31} + \mathbf{H}_{32}$) in the interaction Hamiltonian. It follows from symmetry considerations that not all these terms have to be necessarily present in all cases. The \mathbf{H}_{31} terms are usually denoted as higher-order Coriolis terms [16] (like all terms which are linear in rotational angular momentum). Possible higher-order anharmonic and rovibrational interactions in which a fundamental

vibration could be involved were thus not included in the present work.

The order of magnitude of the coefficients X_i^{mn} of a Hamiltonian term \mathbf{H}_{mn} is $\kappa^{m+2n-4} B \approx \kappa^{m+2n-2} \omega_{vib}$, where $\kappa \approx (D/B)^{1/4} \approx (B/\omega_{vib})^{1/2}$ is a smallness parameter and D, B, ω_{vib} are typical values of the quartic centrifugal distortion constant, rotational constant and harmonic frequency for a molecule in question.

Hence, the order of magnitude for the anharmonic terms is

$$\mathbf{H}_{30} \approx \kappa \omega_{vib}, \quad \mathbf{H}_{31} \approx \kappa^3 \omega_{vib}, \quad \mathbf{H}_{32} \approx \kappa^5 \omega_{vib} \quad (5)$$

The matrix elements of the different interaction terms are given in Appendix B. The correspondence with constants used in previous studies dealing with such anharmonic resonances is given in Table 1.

2.2. Transformed Hamiltonian

The effective Hamiltonian (1) could in principle be diagonalized numerically, and its coefficients X_i^{mn} could be optimized by a least-squares procedure. But before doing this, we have to consider also the limitations due to possible indeterminacies which may result in high correlations between certain parameters.

In fact, as shown by Watson [1,2], the problem is there are infinitely many such Hamiltonians, having the same eigenvalues, but with different values of the X_i^{mn} parameters.

Table 1

Constants used in the literature for the description of the anharmonic resonances.

	This paper	Previous works
2. $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$	$\frac{3}{4}k_{n2n'}$	W_{122} [21,22], W_F [23]
	$\frac{3}{4}k_{n2n'}^J$	W_{122}^J [21,22]
	$\frac{3}{4}k_{n2n'}^K$	W_{122}^K [21,22]
3. $v_n(A_1) \leftrightarrow v_{n'} + v_t(E)$	$2f_{31}$	$-\frac{1}{2}R_{125}^B$ [21,22]
	$2f_{32}^{\sigma z}$	$\frac{1}{2}Y_{125}$ [22]
	$2f_{32}^{\sigma y}$	$\frac{1}{2}X_{125}$ [22]
5. $v_n(A_1) \leftrightarrow 2v_t(A_1 + E)$	$\frac{3}{8}\sqrt{2}k_{n2ta}$	W_{155} [21,22]
	$\frac{3}{8}\sqrt{2}k_{n2ta}^J$	W_{155}^J [21,22]
	$\frac{3}{8}\sqrt{2}k_{n2ta}^K$	W_{155}^K [21,22]
	$2f_{31}^{\sigma z}$	$-\frac{1}{2}R_{155E}^B$ [21,22]
	$2f_{32}^{\sigma z}$	Y_{155} [22]
	$2f_{32}^{\sigma y}$	X_{155} [22]
6. $v_t(E) \leftrightarrow v_{n'} + v_t(E)$	$\frac{3}{4}\sqrt{2}k_{nta'a}$	W_{245}^F [24–26], W_{245} [21,22]
	$\sqrt{2}f_{31}^{\sigma z}$	$\frac{1}{\sqrt{2}}R_{245}^A$ [21,22]
	$\sqrt{2}f_{31}^{\sigma x}$	$-\frac{1}{\sqrt{2}}R_{245}^B$ [21,22]
	$\frac{3}{4}\sqrt{2}k_{nta'a}^J$	W_{245}^J [21,22]
	$\frac{3}{4}\sqrt{2}k_{nta'a}^K$	W_{245}^K [21,22]
	$\sqrt{2}f_{32}^{\sigma z}$	$\frac{1}{\sqrt{2}}Y_{245}$ [22]
8. $v_t(E) \leftrightarrow 2v_n(A_1)$	$\sqrt{2}f_{31}^{\sigma z}$	$-\frac{1}{\sqrt{2}}R_{224}^B$ [21,22]
	$2\sqrt{2}f_{32}^{\sigma z}$	$\frac{1}{\sqrt{2}}Y_{224}$ [22]
	$2\sqrt{2}f_{32}^{\sigma y}$	$\frac{1}{\sqrt{2}}X_{224}$ [22]
9. $v_t(E) \leftrightarrow v_{t'} + v_{t''}(A_1 + A_2 + E)$	$\frac{3}{2}k_{ta't'a}$	W_{7810} [27]
10. $v_t(E) \leftrightarrow 2v_{t'}(A_1 + E)$	$\frac{3\sqrt{2}}{4}k_{t\alpha 2t'a}$	W_{455} [21,22]
	$\frac{3\sqrt{2}}{4}k_{t\alpha 2t'a}^J$	W_{455}^J [21,22]
	$\frac{3\sqrt{2}}{4}k_{t\alpha 2t'a}^K$	W_{455}^K [21,22]
	$\sqrt{2}f_{31}^{\sigma z}$	$\sqrt{2}R_{455E}^A$ [21,22]
	$f_{31}^{\sigma a}$	R_{455A}^B [21,22], R_{455} [28]
	$\sqrt{2}f_{31}^{\sigma b}$	$\sqrt{2}R_{455E}^B$ [21,22]
	$f_{32}^{\sigma za}$	Y_{455} [22]
	$\sqrt{2}f_{32}^{\sigma zb}$	$\sqrt{2}T_{455}$ [22]
	$f_{32}^{\sigma xa}$	X_{455} [22]
	$\sqrt{2}f_{32}^{\sigma xb}$	$\sqrt{2}S_{455}$ [22]

These Hamiltonians may be viewed as connected by unitary contact transformations $\mathbf{U} = e^{i\mathbf{S}}$:

$$\tilde{\mathbf{H}} = \exp(i\mathbf{S})\mathbf{H}\exp(-i\mathbf{S}) = \mathbf{H} + [i\mathbf{S}, \mathbf{H}] + \frac{1}{2}[i\mathbf{S}, [i\mathbf{S}, \mathbf{H}]] + \dots \quad (6)$$

The block diagonal operator \mathbf{S} , which must be Hermitian, invariant to the all operations of the molecular symmetry group and change sign under the time-reversal operation, can be written as a sum of products of the vibrational (V_i) and rotational (R_i) operator parts multiplied by free coefficients s_i

$$\mathbf{S} = \sum_i s_i V_i(\mathcal{L}_n^\pm, \mathcal{L}_{t\pm}^\pm) R_i(\mathbf{J}^\pm, \mathbf{J}_\pm, \mathbf{J}_2), \quad (7)$$

and the free parameters s_i appear in the transformed molecular parameters \tilde{X}_j

$$\tilde{X}_j = X_j + \Delta X_j \quad (s_1, s_2, \dots, s_n) \quad (8)$$

This is the reason the molecular parameters may be highly correlated and cannot be all fitted independently. The values of the free parameters s_i can be fixed by constraining one or more spectroscopic parameters to predetermined values (usually to zero). This procedure is called **reduction**.

In the case of two interacting vibrational states, we will have the standard transformation operators for the quasi-diagonal blocks (belonging to the fundamental and the overtone or the combination bands), which have been described in detail elsewhere [3,4,9,10]. For the interaction block we have found that at this level of approximation it is enough to consider \mathbf{S}_{30} and \mathbf{S}_{31} operators, the parameters of which must satisfy the order of magnitude requirements [3,4,10]

$$s_{30} \approx \kappa^1, \quad s_{31} \approx \kappa^3. \quad (9)$$

The transformation operators are listed together with the Hamiltonian terms in Appendix A. A MAPLE program [6] has been applied to evaluate the commutators in Eq. (6).

For the description of the nondegenerate fundamental v_n , overtone $2v_n$, and combination $v_{n'} + v_{n''}$ bands, it was necessary to include the \mathbf{H}_{40} term, which may be transformed by the \mathbf{S}_{30} operator. For the degenerate overtone $2v_{t'}(A_1 + E)$ and combination $v_{t'} + v_{t''}(A_1 + A_2 + E)$ bands, it was necessary to consider explicitly both the \mathbf{H}_{40} and \mathbf{H}_{41} Hamiltonian terms [12,15], which may be transformed by the contact transformation operators $\mathbf{S}_{30}, \mathbf{S}_{31}$.

As a general rule, we can conclude that the \mathbf{H}_{20} and \mathbf{H}_{40} ‘‘diagonal’’ operators are transformed whenever the Fermi operators \mathbf{H}_{30} and \mathbf{S}_{30} are present.

We recommend however for the parameters in the ‘‘quasi-diagonal’’ blocks to employ in priority the reductions described in detail in Refs. [3,12,15].

After the application of the contact transformation, the molecular parameters become functions of the transformation operator parameters, as shown in Eq. (8). The transformation equations are given in Appendix C.

The constants $A, B, A_\zeta, q_{12}, q_{22}, \alpha_n^A, \alpha_t^A, \alpha_n^B, \alpha_t^B$ have their usual meaning. The parameter s appears already in the case of a degenerate band (fundamental, overtone or a component of the combination band) and has the meaning defined in Refs. [3,6]. It belongs to the transformation operator

$$i\mathbf{S}_{21} = s(\ell_{+2}\mathbf{J}_+ - \ell_{-2}\mathbf{J}_-) \quad (10)$$

where we have used the same abbreviations as in our previous work [9] $\ell_{+2} = \mathcal{L}_{t+}^+, \mathcal{L}_{t+}^-, \ell_{-2} = \mathcal{L}_{t-}^-, \mathcal{L}_{t-}^+$.

The unprimed, primed and double primed parameters belong to a fundamental, overtone or a component of the combination band and correspond to the labeling used in the above description of the studied interactions.

The terms containing the vibration energy differences between the interacting bands are omitted in the transformation equations [6]. They formally satisfy the correct order of magnitude, but in the case of a close resonance the vibration energy difference term is not of the order of ω_{vib} and therefore all these terms can be neglected.

2.3. Reduction schemes

The values of the parameters s, s', s'' appearing in the transformation equations are assumed to be fixed by the reductions in the quasi-diagonal blocks such as the *Q-Reduction*, the *D-Reduction* [3] or the *L-Reduction* [12].

The parameters of the \mathbf{S}_{30} and \mathbf{S}_{31} operators have to be determined by appropriate constraints in the interaction blocks. Now we will specify the reduction schemes for the individual studied resonance cases.

1. $v_n(A_1) \leftrightarrow v_{n'} + v_{n''}(A_1)$

The parameter s_{30} has to be determined by constraining either $k_{nn'n''}^J = 0$ or $k_{nn'n''}^K = 0$. The parameters to be included in the fit are either $k_{nn'n''}^J$ with $k_{nn'n''}^J$ or $k_{nn'n''}^K$ with $k_{nn'n''}^K$.

2. $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$

The parameter s_{30} has to be determined by constraining either $k_{n2n'}^J = 0$ or $k_{n2n'}^K = 0$. The parameters to be included in the fit are either $k_{n2n'}$ with $k_{n2n'}^J$ or $k_{n2n'}$ with $k_{n2n'}^K$.

Table 2
Reduction schemes (sets of parameters to be used in fitting spectra) for the studied cases of Fermi resonance.

	Reduction scheme I	Reduction scheme II
1. $v_n(A_1) \leftrightarrow v_{n'} + v_{n''}(A_1)$	$k_{nn'n''}^J, k_{nn'n''}^K$	$k_{nn'n''}^J, k_{nn'n''}^K$
2. $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$	$k_{n2n'}^J, k_{n2n'}^K$	$k_{n2n'}^J, k_{n2n'}^K$
3. $v_n(A_1) \leftrightarrow v_{n'} + v_{t'}(E)$	f_{31}^x, f_{32}^{xy}	
4. $v_n(A_1) \leftrightarrow v_{t'} + v_{t''}(A_1 + A_2 + E)$	$k_{ntat'a}, k_{ntat'a}^J, f_{31}^x, f_{32}^{xy}$ fails if $(A_\zeta - A_\zeta')$ is ‘small’	$k_{ntat'a}, k_{ntat'a}^J, k_{ntat'a}^K, f_{31}^x, f_{31}^x$
5. $v_n(A_1) \leftrightarrow 2v_{t'}(A_1 + E)$	$k_{n2ta}, k_{n2ta}^J, k_{n2ta}^K, f_{31}^x$ fails if q_t is ‘small’	$k_{n2ta}, k_{n2ta}^J, f_{31}^x, f_{32}^{xy}$ or $k_{n2ta}, k_{n2ta}^K, f_{31}^x, f_{32}^{xy}$
6. $v_{t'}(E) \leftrightarrow v_{n'} + v_{t'}(E)$	$k_{ntat'a}, k_{ntat'a}^J, f_{31}^x, f_{32}^{xy}$ fails if $(A_\zeta - A_\zeta')$ is ‘small’	$k_{ntat'a}, k_{ntat'a}^J, k_{ntat'a}^K, f_{31}^x, f_{31}^x$
7. $v_{t'}(E) \leftrightarrow v_n + v_{n'}(A_1)$	f_{31}^x, f_{32}^{xy}	
8. $v_{t'}(E) \leftrightarrow 2v_{n'}(A_1)$	f_{31}^x, f_{32}^{xy}	
9. $v_{t'}(E) \leftrightarrow v_{t'} + v_{t''}(A_1 + A_2 + E)$	$k_{tat'at'a}, k_{tat'at'a}^J, f_{31}^x, f_{31}^{xb}, f_{31}^{xc}, f_{31}^{xxa}, f_{31}^{xxb}, f_{31}^{xyc}$	$k_{tat'at'a}, f_{31}^x, f_{31}^{xa}, f_{31}^{xb}, f_{31}^{xc}, f_{31}^{xxa}, f_{31}^{xxb}, f_{31}^{xyc}$
10. $v_{t'}(E) \leftrightarrow 2v_{t'}(A_1 + E)$	$k_{ta2t'a}, k_{ta2t'a}^J, f_{31}^x, f_{31}^{xb}, f_{31}^{xxa}, f_{31}^{xxb}, f_{31}^{xyc}$	$k_{ta2t'a}, f_{31}^x, f_{31}^{xa}, f_{31}^{xb}, f_{31}^{xxa}, f_{31}^{xxb}, f_{31}^{xyc}$

3. $v_n(A_1) \leftrightarrow v_{n'} + v_t(E)$
The parameter s_{31} has to be determined by setting $\tilde{f}_{32}^z = 0$. So, at the level of approximation considered in this work, the parameters remaining in the fit are f_{31} and \tilde{f}_{32}^{xy} .
4. $v_n(A_1) \leftrightarrow v_t + v_{t'}(A_1 + A_2 + E)$
The reduction schemes in this case are very similar to those already published in Ref. [6].
The parameter s_{30} has to be determined by setting $\tilde{f}_{31}^z = 0$, the parameter s_{31}^z by setting $\tilde{k}_{ntat'a}^K = 0$, the parameter s_{31}^x by setting $\tilde{f}_{32}^{xz} = 0$. The parameters remaining in the fit are $k_{ntat'a}, k_{ntat'a}^J, f_{31}^x, f_{32}^{xy}$.
In the case, when $(A_\zeta - A_{\zeta'})$ is accidentally very small, the parameter s_{30} has to be determined by the constraint $\tilde{f}_{32}^{xy} = 0$ and the parameter s_{31}^z by constraints in higher order terms (e.g. the parameter $\tilde{R}_{tt'}$ in \mathbf{H}_{42} [15]). The parameters included in the fit are $k_{ntat'a}, k_{ntat'a}^J, k_{ntat'a}^K, f_{31}^z, f_{31}^x$.
In principle, s_{30} could also be determined by the alternative constraint $\tilde{R}_{tt'} = 0$.
5. $v_n(A_1) \leftrightarrow 2v_t(A_1 + E)$
The parameter s_{30} has to be determined by setting $\tilde{f}_{32}^{xy} = 0$, the parameter s_{31}^x by setting $\tilde{f}_{32}^{xz} = 0$. The parameters included in the fit are $k_{n2ta}, k_{n2ta}^J, k_{n2ta}^K, f_{31}^x$.
The constraint $\tilde{f}_{32}^{xy} = 0$ fails when q_t is accidentally small. In this case, we can use one of the constraints $\tilde{k}_{n2ta}^J = 0$ or $\tilde{k}_{n2ta}^K = 0$ to fix s_{30} .
In principle, we can also use the constraint $\tilde{q}_{12}^J = 0$ to determine s_{30} , but we prefer the possibility to use this constraint according to the reduction schemes given in Ref. [12].
The constraint $\tilde{f}_{32}^{xz} = 0$, suggested in order to fix s_{31}^x , fails when $A - B + 2A_{\zeta t}$ is accidentally small. In this case, we suggest the use of the alternative constraint $\tilde{q}_{12}^J = 0$.
6. $v_t(E) \leftrightarrow v_n + v_{t'}(E)$
The reductions for this case were already described in detail in Ref. [6].
One should use in the fit the set of parameters $k_{ntat'a}, k_{ntat'a}^J, f_{31}^x, f_{32}^{xy}$. If $(A_\zeta - A_{\zeta'})$ is accidentally small, the set of parameters to use is $k_{ntat'a}, k_{ntat'a}^J, k_{ntat'a}^K, f_{31}^x, f_{31}^z$.
The interaction case 6 is nicely illustrated in Ref. [18], on the Fermi-interacting $v_4/v_3 + v_6$ bands of deuterated fluorofrom (DCF₃). Here, the authors preferred using a slightly different version of the first reduction scheme proposed in the present work. In this study, the refined parameters were $k_{ntat'a}, k_{ntat'a}^J, f_{31}^x$, and $d_{ntt'}$. The authors found indeed that a slightly better reproduction of the experimental data was achieved when refining the $d_{ntt'}$ $\Delta k = \pm 3$ interaction parameter, from the fourth-order \mathbf{H}_{33} term, rather than the f_{32}^{xy} parameter from the third-order \mathbf{H}_{32} term. This somewhat higher significance of the higher-order $d_{ntt'}$ term over the lower-order ones f_{32}^{xy}, f_{31}^z was explained there by the observed resonant crossings of levels coupled by the $\Delta k = \pm 3$ interaction, whereas the inter-vibrational $\Delta k = \Delta l = \pm 2$ interaction (described by f_{32}^{xy}) is tuned out from resonance by the coincidence with the Fermi crossing. This interaction case could even be recently extrapolated to the $v_3 + v_4/2v_3 + v_6$ band system of the same molecule [19]. In this latter study, the refined parameters were $k_{ntat'a}, k_{ntat'a}^J, f_{31}^x, f_{32}^{xy}$, which strictly corresponds to our first reduction scheme. The obtained values of parameters show a good agreement with those of the $v_4/v_3 + v_6$ lower system.
7. $v_t(E) \leftrightarrow v_n + v_{n'}(A_1)$
8. $v_t(E) \leftrightarrow 2v_n(A_1)$
Cases 7 and 8 are very similar. The parameter s_{31} can be fixed by setting $\tilde{f}_{32}^{xz} = 0$, while the parameters f_{31}^x (which is unaffected) and f_{32}^{xy} remain in the fit.

Table 3
Summary of transformed parameters and possible constraints for the ten cases of interacting levels.

Case No.	Transformed parameter	Depends on	Can be constrained to define	Fails for too small values of	
1	$\tilde{k}_{nn'n''}^J$	s_{30}	s_{30}		
	$\tilde{k}_{nn'n''}^K$	s_{30}	s_{30}		
2	$\tilde{k}_{n2n'}^J$	s_{30}	s_{30}		
	$\tilde{k}_{n2n'}^K$	s_{30}	s_{30}		
3	\tilde{f}_{32}^{xy}	s			
	\tilde{f}_{32}^{xz}	s_{31}	s_{31}		
4	$\tilde{R}_{tt'}$	s_{30}			
	\tilde{f}_{31}^z	s_{30}	s_{30}	$A_\zeta - A_{\zeta'}$	
	\tilde{f}_{31}^x	s, s'			
	$\tilde{k}_{ntat'a}^J$	s_{30}, s, s'	s_{30}		
	$\tilde{k}_{ntat'a}^K$	s_{30}, s_{31}^z, s, s'	s_{31}^z	$A_\zeta - A_{\zeta'}$	
5	\tilde{f}_{32}^{xz}	s_{30}, s_{31}^x, s, s'	s_{31}^x		
	\tilde{f}_{32}^{xy}	s_{30}	s_{30}		
	\tilde{f}_{31}^x	s			
	\tilde{k}_{n2ta}^J	s_{30}, s	s_{30}		
	\tilde{k}_{n2ta}^K	s_{30}, s	s_{30}		
6	\tilde{f}_{32}^{xz}	s_{30}, s_{31}^x, s	s_{31}^x	$A - B + 2A_\zeta$	
	\tilde{f}_{32}^{xy}	s_{30}	s_{30}	q_{22}	
	\tilde{q}_{12}^J	s_{30}, s_{31}^z, s	s_{31}^z		
	\tilde{f}_{31}^z	s_{30}	s_{30}	$A_\zeta - A_{\zeta'}$	
	\tilde{f}_{31}^x	s, s'			
	$\tilde{k}_{ntat'a}^J$	s_{30}, s, s'	s_{30}		
	$\tilde{k}_{ntat'a}^K$	s_{30}, s_{31}^z, s, s'	$\begin{cases} s_{30} \\ s_{31}^z \end{cases}$	$\begin{cases} - \\ A_\zeta - A_{\zeta'} \end{cases}$	
	\tilde{f}_{32}^{xz}	s_{30}, s_{31}^z, s, s'	s_{31}^z		
7	\tilde{f}_{32}^{xy}	s			
	\tilde{f}_{32}^{xz}	s_{31}	s_{31}		
8	\tilde{f}_{32}^{xy}	s			
	\tilde{f}_{31}^z	s_{30}	s_{30}	$A_\zeta + A_{\zeta'} + A_{\zeta''}$	
	\tilde{f}_{31}^x	s''			
	\tilde{f}_{31}^{xb}	s'			
	\tilde{f}_{31}^{xc}	s			
	$\tilde{k}_{ta'ta''a}^J$	s_{30}, s, s', s''	s_{30}		
	$\tilde{k}_{ta'ta''a}^K$	$s_{30}, s_{31}^z, s, s', s''$	s_{31}^z	$A_\zeta + A_{\zeta'} + A_{\zeta''}$	
	\tilde{f}_{32}^{xza}	s_{30}, s'', s_{31}^a	s_{31}^a		
	\tilde{f}_{32}^{xzb}	s_{30}, s', s_{31}^{xb}	s_{31}^{xb}		
	\tilde{f}_{32}^{xzc}	s_{30}, s, s_{31}^{xc}	s_{31}^{xc}		
	\tilde{f}_{32}^{xxa}	s, s', s_{30}			
	\tilde{f}_{32}^{xxb}	s, s'', s_{30}			
	\tilde{f}_{32}^{xyc}	s', s'', s_{30}			
	10	\tilde{q}_{12}^J	s_{30}, s', s_{31}^a		
		\tilde{f}_{31}^z	s_{30}	s_{30}	$A_\zeta + 2A_{\zeta'}$
\tilde{f}_{31}^x		s'			
\tilde{f}_{31}^{xb}		s			
$\tilde{k}_{ta2t'a}^J$		s_{30}, s, s'	s_{30}		
$\tilde{k}_{ta2t'a}^K$		s_{30}, s, s', s_{31}^z	s_{31}^z	$A_\zeta + 2A_{\zeta'}$	
\tilde{f}_{32}^{xza}		s_{30}, s', s_{31}^a	s_{31}^a	$A - B - A_\zeta$	
\tilde{f}_{32}^{xzb}	s_{30}, s, s_{31}^{xb}	s_{31}^{xb}	$A - B + A_\zeta - 2A_{\zeta'}$		
\tilde{f}_{32}^{xxa}	s_{30}, s, s'				
\tilde{f}_{32}^{xyc}	s_{30}, s'				

Table 4
Molecular parameters of DCF_3 (in cm^{-1}) in the ground, $v_5 = 1$, and $v_6 = 2$ ($l = 0, \pm 2$) vibrational states. The interaction scheme corresponds to the case No. 10 discussed above.

Parameter	Ground state ^a	$v_5 = 1$	$v_6 = 2, l = 0$	$v_6 = 2, l = \pm 2$
E	0	975.50827198(33)	1004.060254(26)	1005.983769(13)
B	0.3309331091	0.330621986(30)	0.331094256(99)	0.331060474(48)
C	0.18924413	0.189243978(22)	0.188516535(97)	0.188537096(64)
$D_J \times 10^7$	3.198603	3.21835(16)	3.26761(67)	3.24476(24)
$D_{JK} \times 10^7$	-4.89265	-4.80400(21)	-5.2271(15)	-5.03126(63)
$D_K \times 10^7$	2.1789	2.09655(37)	2.4381(17)	2.23871(82)
$H_J \times 10^{12}$	0.4745	0.4428(15)	0.4745 ^c	0.4745 ^c
$H_{JK} \times 10^{12}$	-2.0065	-1.9663(99)	-2.366(55)	-2.454(18)
$H_{KJ} \times 10^{12}$	2.5994	3.369(16)	3.016(75)	2.924(35)
$H_K \times 10^{12}$	-1.0496	-2.266(13)	-1.0496 ^c	-1.0496 ^c
$C\zeta$		0.138488990(56)		-0.14155297(16)
$\eta_J \times 10^6$		1.64056(61)		-1.12515(64)
$\eta_K \times 10^6$		-1.56895(81)		0.89865(75)
$\tau_J \times 10^{12}$		-10.53(32)		
$\tau_{JK} \times 10^{10}$		2.1181(42)		
$\tau_K \times 10^{10}$		-2.3447(34)		
$q_{22} \times 10^4$		-0.198137(51)	-2.64109(14)	
$f_{22}^J \times 10^{10}$		9.106(28)	10.133(88)	
$f_{22}^K \times 10^{10}$		0.	-10.002(88)	
$f_{42} \times 10^{10}$		-5.5740(23)		
$d_t \times 10^7$		4.1790(34)	-1.088378 ^d	-1.088378 ^d
$d_t^J \times 10^{12}$		2.6011 ^b		
$h_3 \times 10^{14}$	-7.4939	-7.4939 ^c		
$h_3^J \times 10^{19}$	4.77	4.77 ^c		
$q_{12l} \times 10^4$			-1.327(86)	
$f_{31}^{xa} \times 10^3$		-3.785(32)		
$f_{33}^{xaj} \times 10^7$		-3.45(14)		
$f_{33}^{xak} \times 10^6$		5.345 ^e		
$f_{31}^{xb} \times 10^3$		-7.299(28)		
$f_{33}^{xbj} \times 10^7$		-8.09(14)		
$f_{33}^{xbk} \times 10^6$		1.044 ^e		
$f_{32}^{xxa} \times 10^5$		-3.28 ^e		
$f_{32}^{xxb} \times 10^5$		0.9486(24)		
$k_{ta2r'a}$		-1.442 ^e		
$\sigma \times 10^4$		2.23 (2.26) ^f	2.41 (2.41) ^f	2.62 (2.65) ^f

Numbers in parentheses are standard deviations in units of the last digit quoted.

^a Ref. [29].

^b Constrained to a value quoted in Ref. [30].

^c Constrained to the corresponding ground state values, Ref. [29].

^d Constrained to the corresponding $v_6 = 1$ value, quoted in Ref. [29].

^e Constrained to a value from Ref. [20].

^f Standard deviations obtained in Ref. [20] are given in parentheses.

9. $v_t(E) \leftrightarrow v_{t'} + v_{t''}(A_1 + A_2 + E)$

The parameter s_{30} has to be determined by setting $\tilde{f}_{31}^z = 0$.

The parameter s_{31}^z has to be determined by setting $\tilde{k}_{ta't'a}^K = 0$. Further, we should set $\tilde{f}_{32}^{xa} = 0$, $\tilde{f}_{32}^{xb} = 0$, $\tilde{f}_{32}^{xc} = 0$ to determine the values of s_{31}^{xa} , s_{31}^{xb} , s_{31}^{xc} . The parameters remaining in the fit are $k_{ta't'a}$, $k_{ta't'a}^J$, f_{31}^{xa} , f_{31}^{xb} , f_{31}^{xc} , f_{32}^{xxa} , f_{32}^{xxb} , f_{32}^{xxc} .

The parameter s_{30} can be alternatively determined from $k_{ta't'a}^J = 0$, but there seems to be no advantage from that.

In this case, the $R_{t't''}$ parameter, which belongs to the \mathbf{H}_{40} term, is unaffected and should always be refined in the fit.

10. $v_t(E) \leftrightarrow 2v_{t'}(A_1 + E)$

The parameter s_{30} has to be determined by setting $\tilde{f}_{31}^z = 0$.

The parameter s_{31}^z has to be determined by setting $\tilde{k}_{ta2r'a}^K = 0$. Further, we should set $\tilde{f}_{32}^{xa} = 0$, $\tilde{f}_{32}^{xb} = 0$ to determine the values of s_{31}^{xa} , s_{31}^{xb} . The parameters remaining in the fit are $k_{ta2r'a}$, $k_{ta2r'a}^J$, f_{31}^{xa} , f_{31}^{xb} , f_{32}^{xxa} , f_{32}^{xxb} .

The parameter s_{30} can be alternatively determined from $k_{ta2r'a}^J = 0$, but there seems to be no advantage from that.

The “diagonal” \mathbf{H}_{20} , \mathbf{H}_{40} , and \mathbf{H}_{41} terms are all affected by the contact transformation (see Appendix C). The corresponding contributions in the contact transformation are given by the interaction term \mathbf{H}_{30} . In principle, we can now use the constraint $\tilde{q}_{12}^l = 0$ to determine s_{30} or s_{31}^z , but we prefer the possibility to use this constraint according to the reduction schemes given in Ref. [12].

The interaction case (10) was recently applied by Ceausu-Velcescu et al. to the $v_5/2v_6$ band system of DCF_3 [20].¹ In this work, the use of two independent Coriolis parameters f_{31}^{xa} and f_{31}^{xb} , which were fitted independently, was crucial for a significant improvement of the convergence of the Hamiltonian. The inter-vibrational interaction parameters which were refined in the fit were thus f_{31}^{xa} , f_{31}^{xb} (and their J -dependent corrections $f_{33}^{xa,J}$, $f_{33}^{xb,J}$), together with f_{32}^{xxa} , f_{32}^{xxb} . The Fermi-interaction parameter was kept fixed to a value which was found to minimize the standard deviation of the fit.

The parameter q_{12}^l [12] was fixed to zero in Ref. [20]. We have performed a new fit in the present work, using the same data set

¹ The \mathbf{H}_{31}^{xa} and \mathbf{H}_{31}^{xb} Hamiltonian terms used in Ref. [20] have opposite sign with respect to those used in the present work.

as in Ref. [20], but with q_{12}^l refined (Table 4). As it can be seen by comparing results given in Table 4 with those presented in Ref. [20] (Tables 3 and 4), refining this parameter does not induce fundamental changes, neither in the vibrational ‘diagonal’ parameters, nor in the inter-vibrational interaction parameters. However, an important improvement of the standard deviation of the f_{42} and d_t parameters in the $v_5 = 1$ vibrational state has to be noticed. For instance, the f_{42} parameter, which was of $-5.57(16) \times 10^{-10} \text{ cm}^{-1}$ (Ref. [20], Table 3), becomes $-5.5740(23) \times 10^{-10} \text{ cm}^{-1}$; at the same time, the d_t parameter changes from $4.1804(76) \times 10^{-7} \text{ cm}^{-1}$ to $4.1790(34) \times 10^{-7} \text{ cm}^{-1}$. In the present work, the f_{32}^{xxa} α -interaction parameter, which corresponds to a non-resonant interaction, was kept fixed to the value obtained in Ref. [20]. A minor improvement of the global standard deviation of the fit can also be observed (see Table 4).

The reduction schemes corresponding to the ten above cases are collected in Table 2. For practical purposes, a summary of variation of parameters and possible constraints for each interaction case is given in Table 3 .

3. Conclusion

In this paper, a general theory including all possible anharmonic and rovibrational interactions between a fundamental vibration and an overtone or a combination vibration in C_{3v} symmetric-top molecules is presented. For each case of interacting states, different

useful reduction schemes of the Hamiltonian are discussed. Some of these reductions have already proved their efficiency in many practical situations.

Acknowledgments

This work was supported by QUASAAR Marie Curie Research Training Network MRTN-CT-2004-512202 and through the Grant Agency of the Czech Academy of Sciences (Grants IAA400400504), Grants of the Ministry of Education, Youth and Sports of the Czech Republic (research programs MSM6046137307 and LC06071).

The work presented in this paper was partly done while one of the authors (K.S.) visited Laboratory of High Resolution Molecular Spectroscopy in Prague. Kamil Sarka would like to thank Prof. Urban for generous hospitality.

The authors would like to thank Dr. Petr Pracna for very useful suggestions and comments.

Appendix A. The interaction Hamiltonians H_{int} and the transformation operators S for particular cases of Fermi resonance in C_3 molecules

The H_{mn} notation, where m is the total power of vibrational operators and n is the total power of rotational operators, has been employed throughout the paper for the Hamiltonian terms. We have used the relevant interaction operators up to H_{32} .

1. Interaction $v_n(A_1) \leftrightarrow v_{n'}(A_1) + v_{n''}(A_1)$

$$\mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K = \frac{3}{8} (\mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathcal{L}_{n''}^- + \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathcal{L}_{n''}^+) [k_{nn'n''} + k_{nn'n''}^J \mathbf{J}^2 + k_{nn'n''}^K \mathbf{J}_z^2]$$

$$\mathbf{S}_{30} = i s_{30} (\mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathcal{L}_{n''}^- - \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathcal{L}_{n''}^+)$$

2. Interaction $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$

$$\mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K = \frac{3}{16} (\mathcal{L}_{n'}^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- + \mathcal{L}_{n'}^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+) [k_{n2n'} + k_{n2n'}^J \mathbf{J}^2 + k_{n2n'}^K \mathbf{J}_z^2]$$

$$\mathbf{S}_{30} = i s_{30} (\mathcal{L}_{n'}^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- - \mathcal{L}_{n'}^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+)$$

3. Interaction $v_n(A_1) \leftrightarrow v_{n'}(A_1) + v_t(E)$

$$\mathbf{H}_{31} = f_{31} (\mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathbf{J}_+ - \mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathbf{J}_- + \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathbf{J}_- - \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathbf{J}_+)$$

$$\mathbf{H}_{32}^{\text{XZ}} = f_{32}^{\text{XZ}} (\mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- [\mathbf{J}_+, \mathbf{J}_z]_+ + \mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- [\mathbf{J}_-, \mathbf{J}_z]_+ + \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ [\mathbf{J}_z, \mathbf{J}_-]_+ + \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ [\mathbf{J}_z, \mathbf{J}_+]_+)$$

$$\mathbf{H}_{32}^{\text{XY}} = f_{32}^{\text{XY}} (\mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathbf{J}_-^2 + \mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathbf{J}_+^2 + \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathbf{J}_+^2 + \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathbf{J}_-^2)$$

$$\mathbf{S}_{31} = i s_{31} (\mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathbf{J}_+ - \mathcal{L}_t^- \mathcal{L}_n^+ \mathcal{L}_{n'}^- \mathbf{J}_- - \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathbf{J}_- + \mathcal{L}_t^+ \mathcal{L}_n^- \mathcal{L}_{n'}^+ \mathbf{J}_+)$$

4. Interaction $v_n(A_1) \leftrightarrow v_t(E) + v_{t'}(E)$

$$\mathbf{H}_{30} = \frac{3}{4} k_{ntat'a} [\mathcal{L}_n^- (\mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ + \mathcal{L}_{t'}^- \mathcal{L}_{t'}^-) + \mathcal{L}_n^+ (\mathcal{L}_{t'}^- \mathcal{L}_{t'}^- + \mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+)]$$

$$\mathbf{H}_{31}^z = f_{31}^z [\mathcal{L}_n^- (\mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ - \mathcal{L}_{t'}^- \mathcal{L}_{t'}^-) + \mathcal{L}_n^+ (\mathcal{L}_{t'}^- \mathcal{L}_{t'}^- - \mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+)] \mathbf{J}_z$$

$$\mathbf{H}_{31}^x = f_{31}^x [\mathcal{L}_n^- (\mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ \mathbf{J}_+ - \mathcal{L}_{t'}^- \mathcal{L}_{t'}^- \mathbf{J}_-) + \mathcal{L}_n^+ (\mathcal{L}_{t'}^- \mathcal{L}_{t'}^- \mathbf{J}_- - \mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ \mathbf{J}_+)]$$

$$\mathbf{H}_{32}^J + \mathbf{H}_{32}^K = \frac{3}{4} [\mathcal{L}_n^- (\mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ + \mathcal{L}_{t'}^- \mathcal{L}_{t'}^-) + \mathcal{L}_n^+ (\mathcal{L}_{t'}^- \mathcal{L}_{t'}^- + \mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+)] [k_{ntat'a}^J \mathbf{J}^2 + k_{ntat'a}^K \mathbf{J}_z^2]$$

$$\mathbf{H}_{32}^{\text{XZ}} = f_{32}^{\text{XZ}} [\mathcal{L}_n^- (\mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ [\mathbf{J}_z, \mathbf{J}_+]_+ + \mathcal{L}_{t'}^- \mathcal{L}_{t'}^- [\mathbf{J}_z, \mathbf{J}_-]_+) + \mathcal{L}_n^+ (\mathcal{L}_{t'}^- \mathcal{L}_{t'}^- [\mathbf{J}_-, \mathbf{J}_z]_+ + \mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ [\mathbf{J}_+, \mathbf{J}_z]_+)]$$

$$\mathbf{H}_{32}^{\text{XY}} = f_{32}^{\text{XY}} [\mathcal{L}_n^- (\mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ \mathbf{J}_-^2 + \mathcal{L}_{t'}^- \mathcal{L}_{t'}^- \mathbf{J}_+^2) + \mathcal{L}_n^+ (\mathcal{L}_{t'}^- \mathcal{L}_{t'}^- \mathbf{J}_+^2 + \mathcal{L}_{t'}^+ \mathcal{L}_{t'}^+ \mathbf{J}_-^2)]$$

(continued on next page)

Appendix B. The matrix elements for the description of particular cases of Fermi resonance in C_{3v} molecules

The notations correspond to Appendix A.

1. Interaction $v_n(A_1) \leftrightarrow v_{n'}(A_1) + v_{n''}(A_1)$

$$\langle v_n = 1, v_{n'} = 0, v_{n''} = 0, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K | v_n = 0, v_{n'} = 1, v_{n''} = 1, J, k \rangle = \frac{3}{4} \sqrt{2} [k_{nn'n''} + k_{nn'n''}^J J(J+1) + k_{nn'n''}^K k^2]$$

2. Interaction $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$

$$\langle v_n = 1, v_{n'} = 0, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K | v_n = 0, v_{n'} = 2, J, k \rangle = \frac{3}{4} [k_{n2n'} + k_{n2n'}^J J(J+1) + k_{n2n'}^K k^2]$$

3. Interaction $v_n(A_1) \leftrightarrow v_{n'}(A_1) + v_t(E)$

$$\langle v_n = 1, v_{n'} = 0, v_t = 0, l_t = 0, J, k \mp 1 | \mathbf{H}_{31} | v_n = 0, v_{n'} = 1, v_t = 1, l_t = \pm 1, J, k \rangle = \pm 2f_{31} \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 1, v_{n'} = 0, v_t = 0, l_t = 0, J, k \mp 1 | \mathbf{H}_{32}^{xz} | v_n = 0, v_{n'} = 1, v_t = 1, l_t = \pm 1, J, k \rangle = 2f_{32}^{xz} (2k \mp 1) \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 1, v_{n'} = 0, v_t = 0, l_t = 0, J, k \pm 2 | \mathbf{H}_{32}^{xy} | v_n = 0, v_{n'} = 1, v_t = 1, l_t = \pm 1, J, k \rangle = 2f_{32}^{xy} \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 2)}$$

4. Interaction $v_n(A_1) \leftrightarrow v_t(E) + v_{t'}(E)$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 1, l_{t'} = \mp 1, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \frac{3}{4} \sqrt{2} [k_{ntat'a} + k_{ntat'a}^J J(J+1) + k_{ntat'a}^K k^2]$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 1, l_{t'} = \mp 1, J, k | \mathbf{H}_{31}^z | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \pm \sqrt{2} f_{31}^z k$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 1, l_{t'} = \pm 1, J, k \mp 1 | \mathbf{H}_{31}^x | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \pm \sqrt{2} f_{31}^x \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 1, l_{t'} = \pm 1, J, k \mp 1 | \mathbf{H}_{32}^{xz} | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \sqrt{2} f_{32}^{xz} (2k \mp 1) \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 1, l_{t'} = \pm 1, J, k \pm 2 | \mathbf{H}_{32}^{xy} | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \sqrt{2} f_{32}^{xy} \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 2)}$$

5. Interaction $v_n(A_1) \leftrightarrow 2v_t(E)$

$$\langle v_n = 0, v_t = 2, l_t = 0, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K | v_n = 1, v_t = 0, l_t = 0, J, k \rangle = \frac{3}{8} \sqrt{2} [k_{n2ta} + k_{n2ta}^J J(J+1) + k_{n2ta}^K k^2]$$

$$\langle v_n = 0, v_t = 2, l_t = \pm 2, J, k \mp 1 | \mathbf{H}_{31}^x | v_n = 1, v_t = 0, l_t = 0, J, k \rangle = \pm 2f_{31}^x \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 0, v_t = 2, l_t = \pm 2, J, k \mp 1 | \mathbf{H}_{32}^{xz} | v_n = 1, v_t = 0, l_t = 0, J, k \rangle = 2f_{32}^{xz} (2k \mp 1) \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 0, v_t = 2, l_t = \pm 2, J, k \pm 2 | \mathbf{H}_{32}^{xy} | v_n = 1, v_t = 0, l_t = 0, J, k \rangle = 2f_{32}^{xy} \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 2)}$$

6. The interaction $v_t(E) \leftrightarrow v_n(A_1) + v_{t'}(E)$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, J, k \rangle = \frac{3}{4} \sqrt{2} [k_{ntat'a} + k_{ntat'a}^J J(J+1) + k_{ntat'a}^K k^2]$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k | \mathbf{H}_{31}^z | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, J, k \rangle = \pm \sqrt{2} f_{31}^z k$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k \mp 1 | \mathbf{H}_{31}^x | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \mp 1, J, k \rangle = \pm \sqrt{2} f_{31}^x \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k \mp 1 | \mathbf{H}_{32}^{xz} | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \mp 1, J, k \rangle = \sqrt{2} f_{32}^{xz} (2k \mp 1) \sqrt{J(J+1) - k(k \mp 1)}$$

$$\begin{aligned} \langle v_n = 0, v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k \pm 2 | \mathbf{H}_{32}^{xy} | v_n = 1, v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \mp 1, J, k \rangle \\ = \sqrt{2} f_{32}^{xy} \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 2)} \end{aligned}$$

7. Interaction $v_t(E) \leftrightarrow v_n(A_1) + v_{n'}(A_1)$

$$\langle v_t = 0, l_t = 0, v_n = 1, v_{n'} = 1, J, k \mp 1 | \mathbf{H}_{31} | v_t = 1, l_t = \pm 1, v_n = 0, v_{n'} = 0, J, k \rangle = \pm 2 f_{31}^x \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_t = 0, l_t = 0, v_n = 1, v_{n'} = 1, J, k \mp 1 | \mathbf{H}_{32}^{xz} | v_t = 1, l_t = \pm 1, v_n = 0, v_{n'} = 0, J, k \rangle = 2 f_{32}^{xz} (2k \mp 1) \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_t = 0, l_t = 0, v_n = 1, v_{n'} = 1, J, k \pm 2 | \mathbf{H}_{32}^{xy} | v_t = 1, l_t = \pm 1, v_n = 0, v_{n'} = 0, J, k \rangle = 2 f_{32}^{xy} \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 2)}$$

8. Interaction $v_t(E) \leftrightarrow 2v_n(A_1)$

$$\langle v_t = 0, l_t = 0, v_n = 2, J, k \mp 1 | \mathbf{H}_{31} | v_t = 1, l_t = \pm 1, v_n = 0, J, k \rangle = \pm 2 \sqrt{2} f_{31}^x \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_t = 0, l_t = 0, v_n = 2, J, k \mp 1 | \mathbf{H}_{32}^{xz} | v_t = 1, l_t = \pm 1, v_n = 0, J, k \rangle = 2 \sqrt{2} f_{32}^{xz} (2k \mp 1) \sqrt{J(J+1) - k(k \mp 1)}$$

$$\langle v_t = 0, l_t = 0, v_n = 2, J, k \pm 2 | \mathbf{H}_{32}^{xy} | v_t = 1, l_t = \pm 1, v_n = 0, J, k \rangle = 2 \sqrt{2} f_{32}^{xy} \sqrt{J(J+1) - k(k \pm 1)} \sqrt{J(J+1) - (k \pm 1)(k \pm 1)}$$

9. Interaction $v_t(E) \leftrightarrow v_{t'}(E) + v_{t''}(E)$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \pm 1, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = \frac{3}{2} \left[k_{tat'at''a} + k_{tat'at''a}^J J(J+1) + k_{tat'at''a}^K k^2 \right]$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \pm 1, J, k | \mathbf{H}_{31}^z$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = \pm f_{31}^z k$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \mp 1, J, k \pm 1 | \mathbf{H}_{31}^{xa}$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = \pm f_{31}^{xa} \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \mp 1, v_{t''} = 1, l_{t''} = \pm 1, J, k \pm 1 | \mathbf{H}_{31}^{xb}$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = \pm f_{31}^{xb} \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \pm 1, J, k \pm 1 | \mathbf{H}_{31}^{xc}$$

$$| v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = \pm f_{31}^{xc} \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \mp 1, J, k \pm 1 | \mathbf{H}_{32}^{xa}$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = f_{32}^{xa} (2k \pm 1) \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \mp 1, v_{t''} = 1, l_{t''} = \pm 1, J, k \pm 1 | \mathbf{H}_{32}^{xb}$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = f_{32}^{xb} (2k \pm 1) \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \pm 1, J, k \pm 1 | \mathbf{H}_{32}^{xc}$$

$$| v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = f_{32}^{xc} (2k \pm 1) \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \mp 1, J, k \mp 2 | \mathbf{H}_{32}^{xa}$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = f_{32}^{xa} \sqrt{J(J+1) - k(k \mp 1)} \sqrt{J(J+1) - (k \mp 1)(k \mp 2)}$$

(continued on next page)

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \mp 1, v_{t''} = 1, l_{t''} = \pm 1, J, k \mp 2 | \mathbf{H}_{32}^{xxb} \rangle$$

$$| v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = f_{32}^{xxb} \sqrt{J(J+1) - k(k \mp 1)} \sqrt{J(J+1) - (k \mp 1)(k \mp 2)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 1, l_{t'} = \pm 1, v_{t''} = 1, l_{t''} = \pm 1, J, k \mp 2 | \mathbf{H}_{32}^{xxc} \rangle$$

$$| v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, v_{t''} = 0, l_{t''} = 0, J, k \rangle = f_{32}^{xxc} \sqrt{J(J+1) - k(k \mp 1)} \sqrt{J(J+1) - (k \mp 1)(k \mp 2)}$$

10. Interaction $v_t(E) \leftrightarrow 2v_{t'}(E)$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = \pm 2, J, k | \mathbf{H}_{30} + \mathbf{H}_{32}^J + \mathbf{H}_{32}^K | v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \frac{3\sqrt{2}}{4} [k_{ta2t'a} + k_{ta2t'a}^J J + 1 + k_{ta2t'a}^K k^2]$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = \pm 2, J, k | \mathbf{H}_{31}^z | v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \pm \sqrt{2} f_{31}^{z2} k$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = 0, J, k \pm 1 | \mathbf{H}_{31}^{xa} | v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \pm f_{31}^{xa} \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = \pm 2, J, k \pm 1 | \mathbf{H}_{31}^{xb} | v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \pm \sqrt{2} f_{31}^{xb} \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = 0, J, k \pm 1 | \mathbf{H}_{32}^{za} | v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = f_{32}^{za} (2k \pm 1) \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = \pm 2, J, k \pm 1 | \mathbf{H}_{32}^{zb} | v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \sqrt{2} f_{32}^{zb} (2k \pm 1) \sqrt{J(J+1) - k(k \pm 1)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = 0, J, k \mp 2 | \mathbf{H}_{32}^{xa} | v_t = 1, l_t = \mp 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = f_{32}^{xa} \sqrt{J(J+1) - k(k \mp 1)} \sqrt{J(J+1) - (k \mp 1)(k \mp 2)}$$

$$\langle v_t = 0, l_t = 0, v_{t'} = 2, l_{t'} = \pm 2, J, k \mp 2 | \mathbf{H}_{32}^{xb} | v_t = 1, l_t = \pm 1, v_{t'} = 0, l_{t'} = 0, J, k \rangle = \sqrt{2} f_{32}^{xb} \sqrt{J(J+1) - k(k \mp 1)} \sqrt{J(J+1) - (k \mp 1)(k \mp 2)}$$

Appendix C. The transformation equations for the molecular parameters for particular cases of Fermi resonance in C_3 molecules

The constants $A, B, A_s^z, q_{12}, q_{22}, \alpha_n^A, \alpha_n^B, \alpha_{n'}^A, \alpha_{n'}^B$ have their usual meaning. The parameters s are those involved in the transformation operators $iS_{21} = s(\mathcal{L}_{t+}^+ \mathcal{L}_{t+}^- \mathbf{J}_+ - \mathcal{L}_{t-}^- \mathcal{L}_{t-}^+ \mathbf{J}_-)$, introduced in Ref. [3].

The 'energy difference' terms are omitted, because in the case of close resonance they do not satisfy the order of magnitude conditions.

1. Interaction $v_n(A_1) \leftrightarrow v_{n'}(A_1) + v_{n''}(A_1)$

\mathbf{H}_{20}

$$\tilde{E}_n = E_n - 6s_{30} k_{nn'n''}$$

\mathbf{H}_{40}

$$\tilde{\chi}_{n'n''} = \chi_{n'n''} + 6s_{30} k_{nn'n''}$$

\mathbf{H}_{30}

$$\tilde{k}_{nn'n''} = k_{nn'n''}$$

\mathbf{H}_{32}

$$\tilde{l}_{nn'n''}^J = l_{nn'n''}^J - \frac{8}{3} s_{30} (\alpha_n^B - \alpha_{n'}^B - \alpha_{n''}^B)$$

$$\tilde{l}_{nn'n''}^K = k_{nn'n''}^K - \frac{8}{3} s_{30} ((\alpha_n^A - \alpha_n^B) - (\alpha_{n'}^A - \alpha_{n'}^B) - (\alpha_{n''}^A - \alpha_{n''}^B))$$

2. Interaction $v_n(A_1) \leftrightarrow 2v_{n'}(A_1)$

\mathbf{H}_{20}

$$\tilde{E}_n = E_n - 6s_{30} k_{n2n'}$$

$$\tilde{E}_{n'} = E_{n'} - 3s_{30} k_{n2n'}$$

H₄₀

$$\tilde{x}_{n'n'} = x_{n'n'} + 3s_{30}k_{n2n'}$$

H₃₀

$$\tilde{k}_{n2n'} = k_{n2n'}$$

H₃₂

$$\tilde{k}_{n2n'J} = k_{n2n'J} - \frac{16}{3}s_{30}(\alpha_n^B - 2\alpha_{n'}^B)$$

$$\tilde{k}_{n2n'K} = k_{n2n'K} - \frac{16}{3}s_{30}((\alpha_n^A - \alpha_n^B) - 2(\alpha_{n'}^A - \alpha_{n'}^B))$$

3. Interaction $v_n(A_1) \leftrightarrow v_{n'}(A_1) + v_t(E)$

H₃₁

$$\tilde{f}_{31} = f_{31}$$

H₃₂

$$\tilde{f}_{32}^{xz} = f_{32}^{xz} - s_{31}(A - B - A\zeta)$$

$$\tilde{f}_{32}^{xy} = f_{32}^{xy} - sf_{31}$$

4. Interaction $v_n(A_1) \leftrightarrow v_t(E) + v_{t'}(E)$

H₂₀

$$\tilde{E}_n = E_n + 6s_{30}k_{ntat'a}$$

H₄₀

$$\tilde{R}_{tt'} = R_{tt'} - 3s_{30}k_{ntat'a}$$

$$\tilde{x}_{tt'} = x_{tt'} - \frac{3}{2}s_{30}k_{ntat'a}$$

$$\tilde{g}_{tt'} = g_{tt'} + \frac{3}{2}s_{30}k_{ntat'a}$$

H₄₁

$$\tilde{q}_{12l} = q_{12l} + \frac{1}{2}s'R_{tt'} - s(A\zeta' + g_{tt'}) - s_{30}f_{31}^x - \frac{3}{4}s_{31}^x k_{ntat'a} - \frac{9}{8}s_{30}(s + s')k_{ntat'a}$$

$$\tilde{q}'_{12l} = q'_{12l} + \frac{1}{2}sR_{tt'} - s'(A\zeta + g_{tt'}) - s_{30}f_{31}^x - \frac{3}{4}s_{31}^x k_{ntat'a} - \frac{9}{8}s_{30}(s + s')k_{ntat'a}$$

H₃₀

$$\tilde{k}_{ntat'a} = k_{ntat'a}$$

H₃₁

$$\tilde{f}_{31}^z = f_{31}^z - 2s_{30}(A\zeta - A\zeta')$$

$$\tilde{f}_{31}^x = f_{31}^x + \frac{3}{4}(s + s')k_{ntat'a}$$

H₃₂

$$\tilde{k}_{ntat'a}^J = k_{ntat'a}^J + \frac{4}{3}s_{30}(\alpha_n^B - \alpha_t^B - \alpha_{t'}^B) - \frac{4}{3}(s + s')f_{31}^x - ss'k_{ntat'a} - \frac{1}{2}(s^2 + s'^2)k_{ntat'a}$$

$$\tilde{k}_{ntat'a}^K = k_{ntat'a}^K - \frac{8}{3}s_{31}^z(A\zeta - A\zeta') + \frac{4}{3}s_{30}((\alpha_n^A - \alpha_n^B) - (\alpha_t^A - \alpha_t^B) - (\alpha_{t'}^A - \alpha_{t'}^B)) + \frac{4}{3}(s + s')f_{31}^x + ss'k_{ntat'a} + \frac{1}{2}(s^2 + s'^2)k_{ntat'a}$$

$$\tilde{f}_{32}^{xz} = f_{32}^{xz} - s_{31}^x(A - B + A\zeta' + A\zeta') + 2s_{30}(q_{12} + q'_{12}) - \frac{1}{2}(s - s')f_{31}^z + \frac{1}{2}ss_{30}(A - B + 3A\zeta - A\zeta') + \frac{1}{2}s's_{30}(A - B + 3A\zeta' - A\zeta)$$

(continued on next page)

$$\tilde{f}_{32}^{xy} = f_{32}^{xy} + 2s_{30}(q_{22} + q'_{22})$$

5. Interaction $v_n(A_1) \leftrightarrow 2v_t(E)$

H₂₀

$$\tilde{E}_n = E_n + \frac{3}{2}s_{30}k_{n2ta}$$

H₄₀

$$\tilde{x}_{tt} = x_{tt} - \frac{3}{8}s_{30}k_{n2ta}$$

$$\tilde{g}_{tt} = g_{tt} + \frac{3}{8}s_{30}k_{n2ta}$$

H₄₁

$$\tilde{q}'_{12} = q'_{12} - \frac{1}{2}s(A\zeta + 2g_{tt}) - \frac{3}{16}s_{31}^x k_{n2ta} - \frac{1}{2}s_{30}f_{31}^x - \frac{9}{32}ss_{30}k_{n2ta}$$

H₃₀

$$\tilde{k}_{n2ta} = k_{n2ta}$$

H₃₁

$$\tilde{f}_{31}^x = f_{31}^x + \frac{3}{8}s k_{n2ta}$$

H₃₂

$$\tilde{k}_{n2ta}^J = k_{n2ta}^J + \frac{8}{3}s_{30}(\alpha_n^B - 2\alpha_t^B) - \frac{32}{3}s f_{31}^x - 2s^2 k_{n2ta}$$

$$\tilde{k}_{n2ta}^K = k_{n2ta}^K + \frac{8}{3}s_{30}((\alpha_n^A - \alpha_n^B) - 2(\alpha_t^A - \alpha_t^B)) + \frac{32}{3}s f_{31}^x + 2s^2 k_{n2ta}$$

$$\tilde{f}_{32}^{xz} = f_{32}^{xz} - s_{31}^x(A - B + 2A\zeta) + 2s_{30}q_{12} + \frac{1}{2}ss_{30}(A - B + 2A\zeta)$$

$$\tilde{f}_{32}^{xy} = f_{32}^{xy} + 2s_{30}q_{22}$$

6. Interaction $v_t(E) \leftrightarrow v_n(A_1) + v_{t'}(E)$

H₂₀

$$\tilde{E}_t = E_t - 3s_{30}k_{ntat'a}$$

H₄₀

$$\tilde{x}_{nt'} = x_{nt'} + 3s_{30}k_{ntat'a}$$

H₃₀

$$\tilde{k}_{ntat'a} = k_{ntat'a}$$

H₃₁

$$\tilde{f}_{31}^z = f_{31}^z + 2s_{30}(A\zeta - A\zeta')$$

$$\tilde{f}_{31}^x = f_{31}^x + \frac{3}{4}(s - s')k_{ntat'a}$$

H₃₂

$$\tilde{k}_{ntat'a}^J = k_{ntat'a}^J + \frac{4}{3}s_{30}(\alpha_t^B - \alpha_n^B - \alpha_{t'}^B) - \frac{4}{3}(s - s')f_{31}^x - \frac{1}{2}(s^2 - s'^2)k_{ntat'a}$$

$$\tilde{k}_{ntat'a}^K = k_{ntat'a}^K + \frac{8}{3}s_{31}^z(A\zeta - A\zeta') + \frac{4}{3}s_{30}((\alpha_t^A - \alpha_{t'}^A) - (\alpha_n^A - \alpha_n^B) - (\alpha_t^A - \alpha_{t'}^B)) + \frac{4}{3}(s - s')f_{31}^x + \frac{1}{2}(s^2 - s'^2)k_{ntat'a}$$

$$\tilde{f}_{32}^{xz} = f_{32}^{xz} + 2s_{31}^x(A - B + A_\zeta + A_{\zeta'}) - 2s_{30}(q_{12} - q'_{12}) - \frac{1}{2}(s + s')f_{31}^z - \frac{1}{2}ss_{30}(A - B + 3A_\zeta - A_{\zeta'}) + \frac{1}{2}s's_{30}(A - B + 3A_{\zeta'} - A_\zeta)$$

$$\tilde{f}_{32}^{xy} = f_{32}^{xy} - 2s_{30}(q_{22} - q'_{22})$$

7. Interaction $v_t(E) \leftrightarrow v_n(A_1) + v_{n'}(A_1)$

H₃₁

$$\tilde{f}_{31}^x = f_{31}^x$$

H₃₂

$$\tilde{f}_{32}^{xz} = f_{32}^{xz} - s_{31}(A - B - A_\zeta)$$

$$\tilde{f}_{32}^{xy} = f_{32}^{xy} - sf_{31}$$

8. Interaction $v_t(E) \leftrightarrow 2v_n(A_1)$

H₃₁

$$\tilde{f}_{31}^x = f_{31}^x$$

H₃₂

$$\tilde{f}_{32}^{xz} = f_{32}^{xz} - s_{31}(A - B - A_\zeta)$$

$$\tilde{f}_{32}^{xy} = f_{32}^{xy} - sf_{31}$$

9. Interaction $v_t(E) \leftrightarrow v_{t'}(E) + v_{t''}(E)$

H₂₀

$$\tilde{E}_t = E_t + 3s_{30}k_{tat'at''a}$$

H₄₀

$$\tilde{R}_{t't''} = R_{t't''}$$

$$\tilde{\chi}_{t't''} = \chi_{t't''} - \frac{3}{2}s_{30}k_{tat'at''a}$$

$$\tilde{g}_{t't''} = g_{t't''} - \frac{3}{2}s_{30}k_{tat'at''a}$$

H₄₁

$$\tilde{q}'_{12l} = q'_{12l} + \frac{1}{2}s''R_{t't''} - s'(A_{\zeta''} + g_{t't''}) - \frac{3}{4}s_{31}^{xb}k_{tat'at''a} - \frac{1}{2}s_{30}f_{31}^{xb} + \frac{9}{8}s's_{30}k_{tat'at''a}$$

$$\tilde{q}''_{12l} = q''_{12l} + \frac{1}{2}s'R_{t't''} - s''(A_{\zeta'} + g_{t't''}) - \frac{3}{4}s_{31}^{xa}k_{tat'at''a} - \frac{1}{2}s_{30}f_{31}^{xa} + \frac{9}{8}s''s_{30}k_{tat'at''a}$$

H₃₀

$$\tilde{k}_{tata'ta''} = k_{tata'ta''}$$

H₃₁

$$\tilde{f}_{31}^z = f_{31}^z - 2s_{30}(A_\zeta + A_{\zeta'} + A_{\zeta''})$$

$$\tilde{f}_{31}^{xa} = f_{31}^{xa} - \frac{3}{2}s''k_{tat'at''a}$$

$$\tilde{f}_{31}^{xb} = f_{31}^{xb} - \frac{3}{2}s'k_{tat'at''a}$$

(continued on next page)

$$\tilde{f}_{31}^{xc} = f_{31}^{xc} + \frac{3}{2} s k_{ta't'a}$$

H₃₂

$$\tilde{k}_{ta't'a}^j = k_{ta't'a}^j + \frac{2}{3} s_{30} (\alpha_t^B - \alpha_{t'}^B - \alpha_{t''}^B) - \frac{2}{3} (s f_{31}^{xc} - s' f_{31}^{xb} - s'' f_{31}^{xa}) - \frac{1}{2} (s^2 + s'^2 + s''^2) k_{ta't'a}$$

$$\tilde{k}_{ta't'a}^K = k_{ta't'a}^K + \frac{2}{3} s_{30} ((\alpha_t^A - \alpha_{t'}^B) - (\alpha_{t'}^A - \alpha_{t''}^B) - (\alpha_{t''}^A - \alpha_{t''}^B)) + \frac{2}{3} (s f_{31}^{xc} - s' f_{31}^{xb} - s'' f_{31}^{xa}) - \frac{4}{3} s_{31}^z (A\zeta + A\zeta' + A\zeta'') + \frac{1}{2} (s^2 + s'^2 + s''^2) k_{ta't'a}$$

$$\tilde{f}_{32}^{xza} = f_{32}^{xza} + s_{31}^{xa} (A - B - A\zeta - A\zeta' + A\zeta'') + 2s_{30} q_{12}'' - \frac{1}{2} s'' f_{31}^z + \frac{1}{2} s'' s_{30} (A - B + A\zeta + A\zeta' + 3A\zeta'')$$

$$\tilde{f}_{32}^{xzb} = f_{32}^{xzb} + s_{31}^{xb} (A - B - A\zeta + A\zeta' - A\zeta'') + 2s_{30} q_{12}' - \frac{1}{2} s' f_{31}^z + \frac{1}{2} s' s_{30} (A - B + A\zeta + 3A\zeta' + A\zeta'')$$

$$\tilde{f}_{32}^{xzc} = f_{32}^{xzc} + s_{31}^{xc} (A - B + A\zeta - A\zeta' - A\zeta'') - 2s_{30} q_{12} + \frac{1}{2} s f_{31}^z - \frac{1}{2} s s_{30} (A - B + 3A\zeta + A\zeta' + A\zeta'')$$

$$\tilde{f}_{32}^{xxa} = f_{32}^{xxa} + 2s_{30} q_{22}'' + s f_{31}^{xb} - s' f_{31}^{xc} - \frac{3}{2} s s'' k_{ta't'a}$$

$$\tilde{f}_{32}^{xxb} = f_{32}^{xxb} + 2s_{30} q_{22}' + s f_{31}^{xa} - s'' f_{31}^{xc} - \frac{3}{2} s s'' k_{ta't'a}$$

$$\tilde{f}_{32}^{xxc} = f_{32}^{xxc} - 2s_{30} q_{22} - s' f_{31}^{xa} - s'' f_{31}^{xb} + \frac{3}{2} s' s'' k_{ta't'a}$$

10. Interaction $v_t(E) \leftrightarrow 2v_{t'}(E)$

H₂₀

$$\tilde{E}_t = E_t + 3s_{30} k_{ta2t'a}$$

$$\tilde{E}_{t'} = E_{t'} + \frac{3}{2} s_{30} k_{ta2t'a}$$

H₄₀

$$\tilde{x}_{t't'} = x_{t't'} - \frac{3}{4} s_{30} k_{ta2t'a}$$

$$\tilde{g}_{t't'} = g_{t't'} - \frac{3}{4} s_{30} k_{ta2t'a}$$

H₄₁

$$\tilde{q}_{12}^j = q_{12}^j - s' g_{t't'} - \frac{1}{2} s' A\zeta' - \frac{3}{16} s_{31}^{xa} k_{ta2t'a} - \frac{1}{4} s_{30} f_{31}^{xa} + \frac{9}{16} s' s_{30} k_{ta2t'a}$$

H₃₀

$$\tilde{k}_{ta2t'a} = k_{ta2t'a}$$

H₃₁

$$\tilde{f}_{31}^z = f_{31}^z - 2s_{30} (A\zeta + 2A\zeta')$$

$$\tilde{f}_{31}^{xa} = f_{31}^{xa} - \frac{3}{2} s' k_{ta2t'a}$$

$$\tilde{f}_{31}^{xb} = f_{31}^{xb} + \frac{3}{4} s k_{ta2t'a}$$

H₃₂

$$\tilde{k}_{ta2t'a}^j = k_{ta2t'a}^j + \frac{4}{3} s_{30} (\alpha_t^B - 2\alpha_{t'}^B) - \frac{4}{3} (s f_{31}^{xb} - s' f_{31}^{xa}) - \frac{1}{2} (s^2 + 2s'^2) k_{ta2t'a}$$

$$\tilde{k}_{ta2t'a}^K = k_{ta2t'a}^K + \frac{4}{3} s_{30} ((\alpha_t^A - \alpha_{t'}^B) - 2(\alpha_{t'}^A - \alpha_{t''}^B)) + \frac{4}{3} (s f_{31}^{xb} - s' f_{31}^{xa}) - \frac{8}{3} s_{31}^z (A\zeta + 2A\zeta') + \frac{1}{2} (s^2 + 2s'^2) k_{ta2t'a}$$

$$\tilde{f}_{32}^{xza} = f_{32}^{xza} + s_{31}^{xa}(A - B - A\zeta) + 4s_{30}q'_{12} - s'f_{31}^z + s's_{30}(A - B + A\zeta + 4A\zeta')$$

$$\tilde{f}_{32}^{xzb} = f_{32}^{xzb} + s_{31}^{xb}(A - B + A\zeta - 2A\zeta') - 2s_{30}q_{12} + \frac{1}{2}sf_{31}^z - \frac{1}{2}ss_{30}(A - B + 3A\zeta + 2A\zeta')$$

$$\tilde{f}_{32}^{xxa} = f_{32}^{xxa} + 4s_{30}q'_{22} - 2s'f_{31}^{xb} + sf_{31}^{xa} - \frac{3}{2}ss'k_{ta2t'a}$$

$$\tilde{f}_{32}^{xxb} = f_{32}^{xxb} - 2s_{30}q_{22} - s'f_{31}^{xa} + \frac{3}{4}s'^2k_{ta2t'a}$$

References

- [1] J.K.G. Watson, *J. Chem. Phys.* 46 (1967) 1935–1949.
- [2] J.K.G. Watson, Aspects of quartic and sextic centrifugal effects on rotational energy levels, in: J. Durig (Ed.), *Vibrational Spectra and Structure*, vol. 6, 1977, pp. 1–89.
- [3] J.K.G. Watson, C. Gerke, H. Harder, K. Sarka, *J. Mol. Spectrosc.* 187 (1998) 131–141.
- [4] E.I. Lobodenko, O.N. Sulakshina, V.I. Perevalov, V.I. Tyuterev, *J. Mol. Spectrosc.* 126 (1987) 159–170.
- [5] V.I. Perevalov, V.I. Tyuterev, *J. Mol. Spectrosc.* 96 (1982) 56–76.
- [6] K. Sarka, L. Nová Střiteská, *J. Mol. Spectrosc.* 257 (2009) 108–110.
- [7] J. Demaison, K. Sarka, E.A. Cohen, *Spectroscopy from space*, NATO Science Series, II Mathematics, Physics and Chemistry, vol. 20, Kluwer Academic Publishers, 2001.
- [8] D. Papoušek, M.R. Aliev, *Studies in Physical and Theoretical Chemistry, Molecular Vibrational–Rotational Spectra, Theory and Applications of High Resolution Infrared, Microwave and Raman Spectroscopy of Polyatomic Molecules*, Vol. 17, 1982, p. 342.
- [9] L. Nová Střiteská, K. Sarka, Š. Urban, *J. Mol. Spectrosc.* 256 (2009) 135–140.
- [10] K. Sarka, D. Papoušek, J. Demaison, H. Mader, H. Harder, *Advan. Ser. Phys. Chem.* (1997) 9 (Vibration–Rotational Spectroscopy and Molecular Dynamics), 116–238..
- [11] K. Sarka, J. Demaison, in: P. Jensen, P.R. Bunker (Eds.), *Computational Molecular Spectroscopy*, Wiley and Sons, New York, 2000.
- [12] K. Sarka, H. Harder, *J. Mol. Spectrosc.* 197 (1999) 254–261.
- [13] G. Graner, *J. Mol. Spectrosc.* 161 (1993) 58–79.
- [14] G. Graner, H. Bürger, *Advan. Ser. Phys. Chem.* 9 (1997) (Vibration–Rotational Spectroscopy and Molecular Dynamics), 239–297..
- [15] A. Ceausu-Velcescu, P. Pracna, L. Nová Střiteská, *J. Mol. Spectrosc.* 289 (2013) 7–12.
- [16] M.R. Aliev, J.K.G. Watson, 3 (1985) 1–67.
- [17] G. Wagner, B.P. Winniewisser, M. Winniewisser, K. Sarka, *J. Mol. Spectrosc.* 162 (1993) 82–119.
- [18] P. Pracna, A. Ceausu-Velcescu, A. Predoi-Cross, Š. Urban, *J. Mol. Spectrosc.* 259 (2010) 1–10.
- [19] A. Ceausu-Velcescu, P. Pracna, *J. Mol. Spectrosc.* 295 (2014) 31–36.
- [20] A. Ceausu-Velcescu, P. Pracna, A. Predoi-Cross, *J. Mol. Spectrosc.* 267 (2011) 150–157.
- [21] J.P. Champion, A.G. Robiette, I.M. Mills, G. Graner, *J. Mol. Spectrosc.* 96 (1982) 422–441.
- [22] M. Badaoui, J.P. Champion, *J. Mol. Spectrosc.* 109 (1985) 402–411.
- [23] Y. Ding, E. Bertseva, H. Bürger, A. Campargue, *J. Mol. Spectrosc.* 220 (2003) 1–6.
- [24] K. Burczyk, H. Bürger, L. Halonen, *J. Mol. Spectrosc.* 159 (1993) 265–273.
- [25] E. Cané, L. Fusina, K. Burczyk, *J. Mol. Spectrosc.* 247 (2008) 57–63.
- [26] E. Cané, L. Fusina, K. Burczyk, *J. Mol. Spectrosc.* 239 (2006) 146–153.
- [27] J.L. Duncan, I.J. Wright, D. Ellis, *J. Mol. Spectrosc.* 37 (1971) 394–407.
- [28] L. Fusina, G. Nivellini, F. Ospitali, F. Tullini, H. Bürger, *J. Mol. Spectrosc.* 246 (2007) 57–64.
- [29] P. Pracna, A. Ceausu-Velcescu, H. Bürger, *J. Mol. Spectrosc.* 250 (2008) 59–69.
- [30] P. Pracna, K. Sarka, J. Demaison, J. Cosléou, F. Herlemont, M. Khelkhal, H. Fichoux, D. Papoušek, M. Papiński, H. Bürger, *J. Mol. Spectrosc.* 184 (1997) 93–105.