Counting levels within vibrational polyads.
Generating function approach.

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Simple analytical formulae for the number of energy levels in the vibrational polyads are given. These formulae account for the resonances between the vibrational modes, and for the symmetry of the problem, so that the number of states of a particular symmetry type can be computed. The formulae are used to estimate the differential and integral densities of states from the minimum initial information about the molecule. Examples of the vibrational structure of triatomic molecules A_3, tetrahedral molecules AB_4, and linear molecules AB_2 are considered. The analytical formulae are compared to the *ab initio* results for H_3^+ [J. R. Henderson *et al.*, J. Chem. Phys. **98**, 7191 (1993)].

Contents

I. INTRODUCTION

The structure of the vibrational energy level system of many polyatomic molecules often exhibits isolated groups of vibrational levels, called vibrational polyads [1–4]. These polyads can be seen clearly when the ratio of the vibrational frequencies is close to a simple rational number. For example, consider a molecule with three vibrational modes. Near

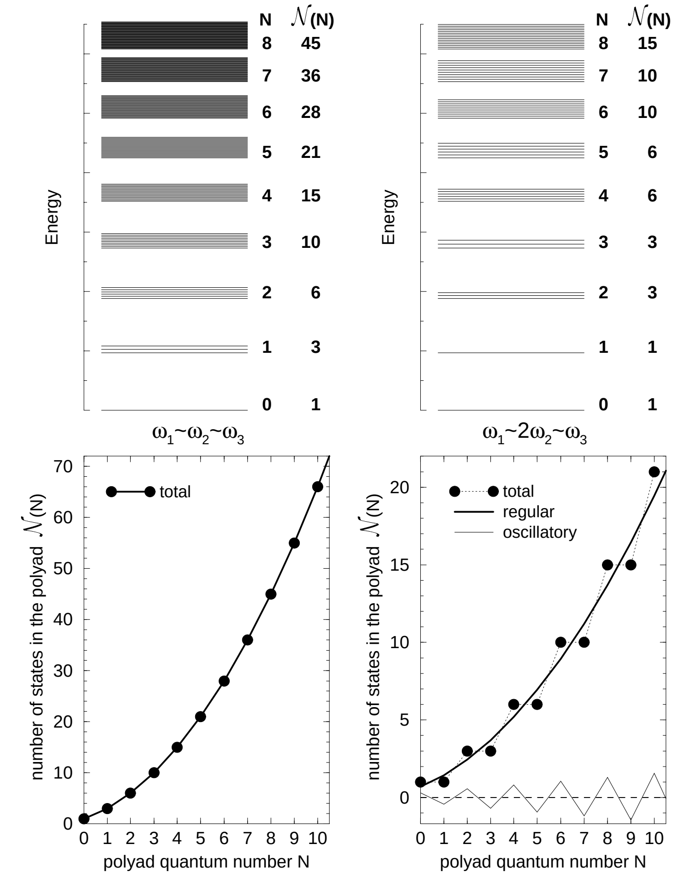

FIG. 1. Vibrational polyads of three-dimensional oscillators and the number of states $\mathcal{N}(N)$. (above) A schematic pattern of polyads. (below) The number of states as function of the polyad quantum number N: circles give the actual number of states, the solid line gives a parabolic approximation, and in the case of $\nu_1 \approx 2\nu_2 \approx \nu_3$ (right), the "oscillatory" part, the difference between the exact numbers and the smooth curve, is shown.

the equilibrium geometry the Hamiltonian of this system can be represented as a Hamiltonian of a three-dimensional anharmonic oscillator with frequencies ν_1, ν_2, and ν_3,

$$H = \tfrac{1}{2}\sum_{i=1}^{3} \nu_i (p_i^2 + q_i^2) + V_{\mathrm{anharmonic}}. \tag{1}$$

In the simplest case of a nearly isotropic oscillator $\nu_1 \approx \nu_2 \approx \nu_3$, and, provided that the anharmonicity V is small, we can clearly see vibrational polyads as shown schematically in Fig. 1, left. If we label these polyads by the polyad quantum number $N = 0, 1, 2, \ldots$, then the number of states (vibrational energy levels) in each polyad $\mathcal{N}(N)$ equals $(N+1)(N+2)/2$. The internal structure of polyads depends strongly on the nature of the anharmonic terms V. For instance, at low N this structure can be well described in terms of normal modes, while at high N the local mode description can be more physically meaningful [5]. On the other hand, the polyads themselves exist for any sufficiently small anharmonic terms V regardless of the actual nature of these terms.

Our purpose is to give a simple formula that can estimate the density of states using *only* the very basic initial information on the molecule, namely the frequencies and the symmetry types of the vibrational modes, and the resonance condition. Describing internal structure of the polyads might be difficult [3], whereas the system of polyads as a whole can be analyzed in much simpler terms. Indeed, if we neglect the splitting of levels within each polyad than the energy of the polyad $E(N)$ can be defined as a function of the polyad quantum number N. In the harmonic approximation $E(N)$ is a linear function. We can introduce nonlinear corrections, such that $E(N) = \nu(1 + a_1 N + a_2 N^2 + \ldots)$, to account for anharmonicity of the real potential [6,7].

Therefore, as long as the polyads exist (N is a good quantum number) and we are not interested in their internal structure, we can obtain a rough estimate of the *average* density of states by calculating the number of states in each polyad. Such an estimate will not display any fluctuations of the density of states due to the internal structure of polyads. Thus, as is well known [8], the average density of states of a three-mode system with three frequencies of the same order of magnitude is a quadratic function of energy, and indeed, the number of states $\mathcal{N}(N)$ shown in Fig. 1 is a polynomial in N of degree 2.

New features of the density of states arise when vibrational frequencies satisfy (approximately) less trivial resonance conditions. For example, let us consider a three-dimensional oscillator with a Fermi resonance $\nu_1 \approx 2\nu_2 \approx \nu_3$ (ratio $\nu_1 : \nu_2 : \nu_3 \approx 2 : 1 : 2$). This oscillator can serve as a zero order approximation to the vibrations of triatomic nonlinear molecules, such as H_2O: the two stretching modes of H_2O, symmetric ν_1 and antisymmetric ν_3, are quasidegenerate, and the frequency of the bending mode ν_2 is roughly one half the frequency of the stretching modes. In this case, the energy gap between the neighboring polyads N and $N+1$ equals approximately $h\nu_2$. As shown below the number of states in the N-th polyad,

$$\mathcal{N}_{2:1:2}(N) = \frac{1}{8}N^2 + \frac{5}{8}N + \frac{11}{16} - \left(N + \frac{5}{2}\right)\frac{(-1)^N}{8}, \tag{2}$$

has a regular part, again a polynomial in N of degree 2, and an oscillatory part $\propto (-1)^N$, shown in Fig. 1, right. Hence, even though we ignore the internal structure of polyads, we still expect the quantum density of states to have oscillations in addition to the general parabolic behavior. Both the oscillations and the coefficients in the regular part become more complicated when we use larger integer numbers $n_1 : n_2 : n_3$ in order to reproduce more precisely the actual ratio $\nu_1 : \nu_2 : \nu_3$. Certainly, expressions become more complex with growing number of vibrational modes (degrees of freedom).

In what follows we derive explicit general formulae for the density of states of a multidimensional quantum oscillator with arbitrary resonance condition $n_1 : n_2 : \cdots n_K$ [cf. formula (2)]. We also take into account the symmetry requirements that should be imposed if the molecule possesses some nontrivial symmetry. For the harmonic oscillator (the zero-order approximation) this problem can be completely solved by purely group-theoretical techniques, known for almost a century [9–11] (see Appendix A). Such explicit formulae have not as yet been obtained and analyzed, and our work intends to cover this gap. The key point is, in our view, that such formulae can be subsequently corrected to give a reliable quantitative estimation of the density of states of the actual anharmonic oscillator. This makes our approach useful for the study of such systems as polyatomic molecules [12], and even for the analysis of "quantum chaos" [13]. In the past the density of states of multidimensional anharmonic oscillators has been studied numerically for various model vibrational Hamiltonians with different symmetry groups [14–21]. The density of states of a given symmetry type for both a multidimensional oscillator system and a quantum billiard with symmetry has been recently calculated using the semiclassical theory [22–24]. We are interested in molecular applications and therefore, we only analyze model vibrational Hamiltonians which can be initially approximated by a harmonic oscillator (small vibrations near the equilibrium).

Resonances between the vibrational modes may be approximate or exact (due to symmetry). Vibrational structure of molecules provides a great number of examples of both kinds. Table I summarizes those molecular examples which we use later in this paper. In each case we consider K vibrational modes with frequencies ν_i, $i = 1, \ldots, K$, and suppose a resonance condition $\nu_1 : \nu_2 : \cdots : \nu_K \approx n_1 : n_2 : \cdots : n_K$. All n_i should be taken as positive integers; they can be large in order to reproduce the ratio of the actual frequencies with desired accuracy. We draw attention to this definition because alternative definitions, with a similar notation, but with a completely different meaning, are possible.

To label the vibrational polyads we introduce the polyad quantum number N. In the simplest interpretation N is just a sequential number (cf. Fig. 1). The physical meaning of the polyad quantum number N can be understood in several ways. In a purely quantum approach, in the limit of uncoupled oscillators (vibrational modes) the definition of N is given in terms of the numbers of quanta in different modes $N_1, N_2, \ldots, N_K$ in accordance with the resonance condition. For instance, the polyads formed by two vibrations $\nu_1 : \nu_2 \approx 2 : 1$, can be characterized by the number $N = 2N_1 + N_2$, with N_1 and N_2 the number of quanta in modes ν_1 and ν_2 [25]. If the two modes couple, N still can remain a good quantum number while N_1 and N_2 can loose their meaning. A corresponding classical interpretation is in terms of total action I and individual actions $I_1, I_2, \ldots, I_K$ [1]. In terms of hyperspherical coordinates N is the quantum number that corresponds to the hyper-radial motion.

The organization of the paper is as follows. In Sec. II we give the formulae for the number of states of multidimensional quantum harmonic oscillators with various resonances. Sec. III shows how to apply the same technique for systems with nontrivial symmetry where it is highly desirable to partition the total number (density) of states into the numbers of states of each symmetry type. Further, in Sec. IV, we discuss the generalization to the more complex rotation-vibration problem. Finally, in Sec. IV D, we show on a convincing example how a simple phenomenological anharmonicity correction to the polyad energy $E(N)$ can bring the results of the harmonic approximation into the good quantitative agreement with the density of states of a real system.

The mathematical technique of this paper is based on the theory of invariants and the use of Molien (generating)

TABLE I. Vibrational resonances in molecules

Molecule	G^{a}	vibrational modes[b] $\nu(\Gamma)_\sigma$	K^{c}	resonance $\nu_1:\nu_2:\cdots:\nu_K$	polyad number N^{d}
AB_2	C_{2v}	$\nu_1(A_1), \nu_2(A_1), \nu_3(B_1)$	3	$n_1 : n_3 : n_2$	
H_2O	(C_2)	ν_1, ν_3	2	1:1	$N_1 + N_3$
	(C_{2v})	ν_1, ν_2, ν_3	3	2:2:1	$2(N_1 + N_3) + N_2$
AB_2	$D_{\infty h}$	$\nu_1(\Sigma_g^+), \nu_2(\Pi_u)_{(x,y)}, \nu_3(\Sigma_u^+)$	4	$n_1 : n_2 : n_2 : n_3$	
CO_2	(C_∞)	ν_1, ν_2	3	2:1:1	$2N_1 + N_2$
CS_2	(C_∞)	ν_1, ν_2	3	5:3:3	$5N_1 + 3N_2$
	$(C_{\infty h})$	ν_1, ν_2, ν_3	4	10:6:6:23	$10N_1 + 6N_2 + 23N_3$
A_3	D_{3h}	$\nu_1(A_1'), \nu_2(E')_{(x,y)}$	3	$n_1 : n_2 : n_2$	
H_3^+	(C_{3v})	ν_1, ν_2	3	5:4:4	$5N_1 + 4N_2$
AB_4	T_d	$\nu_1(A_1), \nu_2(E)_\sigma, \nu_3(F_2)_\sigma, \nu_4(F_2)_\sigma$	9	$n_1 : n_3 : n_3 : n_3 : n_2 : n_2 : n_4 : n_4 : n_4$	
CH_4	(T_d)	$\nu_1, \nu_2, \nu_3, \nu_4$	9	2:2:2:2:1:1:1:1:1	$2(N_1 + N_3) + N_2 + N_4$
SiH_4	(T_d)	ν_1, ν_3	4	1:1:1:1	$N_1 + N_3$
CD_4	(T_d)	ν_2, ν_4	5	1:1:1:1:1	$N_2 + N_4$

[a] Symmetry group and its image in the concrete vibrational representation (in brackets).
[b] For each mode we give spectroscopic notation ν_k, symmetry type Γ, and components σ for degenerate modes; $\sigma = (a, b)$ for E-modes and (x, y, z) for F-modes.
[c] Total number of vibrational degrees of freedom that are considered.
[d] N_i is the number of quanta in mode ν_i.

functions. There are many applications of this technique, for instance in particle physics [26], nuclear physics [27–30], solid state physics [31–33], continuum mechanics [34]. In molecular physics, Molien functions have been used for invariant global description of potential energy surfaces [35–37] and for construction of effective vibration-rotation Hamiltonians in terms of invariant tensor operators [35,38,39]. Since, to our knowledge, this technique has not been applied directly to the calculation of the number and the density of states, it may not be widely known to those who are interested in the results of such applications. In order to present these results in an accessible and concise form we do not go through all the details of the required mathematical techniques in the main body of the paper. Instead, we outline these techniques in the Appendices. Appendix A presents the standard theory needed to construct the Molien functions for different symmetry groups. Concrete examples of finite and continuous groups follow.

In the theory of invariants we consider constructing new invariants (or covariants) as polynomials of degree N in basic invariants. The latter can, for instance, be vibrational wavefunctions corresponding to one-quantum ($N = 1$) single-mode excitations, the so-called fundamentals. Thus, in our three-mode example (1) we would construct wavefunctions $|n_1 n_2 n_3\rangle$ from the three basic functions $|100\rangle$, $|010\rangle$ and $|001\rangle$.

The coefficient of the term of order N in the Taylor expansion of the Molien generating function gives $\mathcal{N}(N)$, the number of invariants (covariants) of degree N. In our case we count the number of totally symmetric vibrational states (invariants) and the number of states of other possible symmetries (covariants). Thus by computing Taylor coefficients we can tabulate numerically the function for the number of states (of given symmetry) $\mathcal{N}(N)$ for all positive integer polyad quantum numbers N. This approach has been always implemented in the theory of invariants. Appendix B summarizes our original method of transforming the generating function into an *explicit* analytic expression for $\mathcal{N}(N)$. In our work the function $\mathcal{N}(N)$ gives the number of states and its analytic form is very useful in the subsequent analysis of the density of states.

Some of our analytical expressions may not be simple to derive and to manipulate by hand. They, however, can be easily handled by symbolic computer algebra programs, such as Maple V used in this work [40].

II. TOTAL NUMBER OF STATES IN A POLYAD

A. Isotropic oscillator

Consider a K-dimensional isotropic harmonic oscillator with frequency [7] $\nu = \nu_1 = \nu_2 = \cdots = \nu_K$, and consider all states with energy $\nu N + \frac{1}{2}\nu K$. This group of states forms a polyad characterized by the quantum number N. Let $\mathcal{N}(N, K)$ be the total number of states in such a polyad. This number equals the number of partitions of N

quanta into K parts [8]. From the group theoretical point of view $\mathcal{N}(N,K)$ is the dimension of the representation of the dynamical symmetry group of the K-dimensional isotropic harmonic oscillator [41], $SU(K)$, characterized by the single-row Young diagram $\square\cdots\square$ with N boxes. It can be given either explicitly

$$\mathcal{N}(N,K) = \frac{K(K+1)(K+2)\ldots(K+N-1)}{N!} \tag{3a}$$
$$= \frac{(N+1)(N+2)\ldots(N+K-1)}{(K-1)!} \tag{3b}$$

or in the form of a generating function depending on an auxiliary variable λ [42]

$$g_K(\lambda) = \frac{1}{(1-\lambda)^K}. \tag{4}$$

To obtain $\mathcal{N}(N,K)$ from the generating function $g_K(\lambda)$ we expand the latter in the power series

$$g_K(\lambda) = C_0 + C_1\lambda + C_2\lambda^2 + \ldots + C_N\lambda^N + \ldots\ . \tag{5}$$

The coefficient before λ^N gives the number of states in the polyad with polyad quantum number N,

$$C_N = \mathcal{N}(N,K). \tag{6}$$

The two alternative representations of $\mathcal{N}(N,K)$ in (3) are equivalent; the form (3b) shows immediately that $\mathcal{N}(N,K)$ is a polynomial in N of degree $(K-1)$.

Lines 1:1 and 1:1:1 in Table II show the generating functions and the total number of states in the polyads for two- and three-dimensional isotropic oscillators ($K=2,3$). For $K=3$ coefficients (6) $C_N = \mathcal{N}(N,3)$ are shown by black circles in Fig. 1, left.

B. Several independent isotropic oscillators

Consider a system that consists of several independent (uncoupled) subsystems. Each of the subsystems $i=1,2,\ldots$, is described by an appropriate isotropic oscillator with K_i modes and polyad quantum number N_i. The groups of levels of the whole system are labeled by the set of quantum numbers $(N_1, N_2, \ldots)$, so that the number of states in such the group $(N_1, N_2, \ldots)$ equals the product $\prod \mathcal{N}(N_i, K_i)$. This number can be easily calculated with the generating function of the whole system, $g(\lambda_1, \lambda_2, \ldots)$, with auxiliary variables $\lambda_1, \lambda_2, \ldots$, corresponding to subsystems $i=1,2,\ldots$. Thus to count the degeneracy of level (N_1, N_2) of a system composed of two subsystems $i=1,2$, with, respectively, K_1 and K_2 modes we introduce the generating function

$$g(\lambda_1,\lambda_2) = g_{K_1}(\lambda_1) g_{K_2}(\lambda_2), \tag{7}$$

with auxiliary variables λ_1 and λ_2 referring to subsystems 1 and 2, and functions g_{K_1} and g_{K_2} defined in Eq. (4). Coefficients C_{N_1,N_2} in the expansion

$$g(\lambda_1,\lambda_2) = \sum_{N_1,N_2} C_{N_1,N_2}\, \lambda_1^{N_1}\lambda_2^{N_2} \tag{8}$$

give the degeneracy of (or the number of states on) the level (N_1, N_2).

For example, the number of states in the groups (polyads) formed by the nondegenerate mode ν_1 and the double degenerate mode ν_2 is described by

$$g(\lambda_1,\lambda_2) = \frac{1}{(1-\lambda_1)(1-\lambda_2)^2}. \tag{9a}$$

[Note that the "polyads" of the onedimensional oscillator (of the nondegenerate mode ν_1) consist each of one level and $\mathcal{N}(N_1, K_1=1) \equiv 1$.] The generating function

$$g(\lambda_1,\lambda_2) = \frac{1}{(1-\lambda_1)^4(1-\lambda_2)^5} \tag{9b}$$

describes a system formed by a four- and a five-dimensional oscillator.

C. Resonances

In the case of resonances we cannot separate our total system into subsystems, each with its own good quantum number N_i. Instead we characterize energy levels by a *single* polyad quantum number N [1–3]. Similarly, instead of auxiliary variables $\lambda_1, \lambda_2, \ldots$, we introduce one variable λ. The relation between λ and $\lambda_1, \lambda_2, \ldots$, and between N and $N_1, N_2, \ldots$, is defined by the resonance. The isotropic oscillator in Sec. II A corresponds to the trivial case of the resonance $\underbrace{1:1:\cdots:1}_{K}$, such that $\lambda = \lambda_1 = \lambda_2 = \ldots = \lambda_K$ and $N = N_1 + N_2 + \ldots + N_K$. Tables I and II show how to apply this idea to other resonances.

Let us return to the example of the three-dimensional oscillator with frequencies ν_1, ν_2, and ν_3 (Sec. I). If all three oscillators are independent we use the generating function

$$g(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{1-\lambda_1}\frac{1}{1-\lambda_2}\frac{1}{1-\lambda_3}. \tag{10}$$

This function bears no structural information on the energy level system because each single level has a unique set of labels N_1, N_2, N_3 and is considered independently. However, if the three modes are in resonance $\nu_1 : \nu_2 : \nu_3 \approx 2:1:2$ they form distinct polyads (Fig. 1, right). To label these polyads we should introduce the polyad quantum number $N = 2N_1 + N_2 + 2N_3$. Now the generating function

$$g_{2:1:2}(\lambda) = \frac{1}{(1-\lambda)(1-\lambda^2)^2} \tag{11}$$

depends on the single auxiliary variable λ, such that $\lambda_1 = \lambda_3 = \lambda^2$ and $\lambda_2 = \lambda$. Coefficients C_N in the Taylor expansion of $g_{2:1:2}(\lambda)$ give the number of states in polyad N (black circles in Fig. 1, right).

In the case of Fermi resonance 2:1:1 of a nondegenerate mode ν_1 and a doubly degenerate mode ν_2, $\nu_1 \approx 2\nu_2$ (CO_2 in Table I) the polyad quantum number is defined as $N = 2N_1 + N_2$, with N_1 and N_2 the numbers of vibrational quanta in modes ν_1 and ν_2. The generating function $g_{2:1:1}(\lambda)$ in Table II is obtained from (9a) by substitution $\lambda_2 = \lambda$ and $\lambda_1 = \lambda^2$. It has factors $(1-\lambda^2)$ and $(1-\lambda)$ in the denominator to account for excitation of modes ν_1 (with higher frequency) and ν_2.

A tetrahedral molecule AB_4 has two stretching modes $\nu_1(A_1)$ and $\nu_3(F_2)$, and two bending modes $\nu_2(E)$ and $\nu_4(F_2)$. Their degeneracies are, respectively, 1, 3, and 2, 3, so that for $\nu_1 \approx \nu_3$ and $\nu_2 \approx \nu_4$ the stretching and bending vibrations are described by the four- and five-dimensional isotropic oscillators with the two parameter generating function (9b). Furthermore, if the bending-to-stretching frequency ratio is 1:2 (CH_4 in Table I) the polyad quantum number is $N = 2(N_1 + N_3) + (N_2 + N_4)$ and the generating function

$$g_{2:2:2:2:1:1:1:1:1}(\lambda) = \frac{1}{(1-\lambda^2)^4(1-\lambda)^5} \tag{12}$$

gives the total number of states in the polyads. Thus, first coefficients in the Taylor expansion of (12)

$$g_{2:2:2:2:1:1:1:1:1}(\lambda) = 1 + 5\lambda + 19\lambda^2 + 55\lambda^3 + \ldots, \tag{13}$$

give the number of vibrational components for polyads with $N = 0$ (ground state), 1, 2, 3, etc. In the spectroscopic literature [43] they are called dyad (ν_2, ν_4), pentad ($2\nu_2$, $2\nu_4$, $\nu_2{+}\nu_4$, ν_1, ν_3), octad ($3\nu_2$, $2\nu_2{+}\nu_4$, $\nu_2{+}2\nu_4$, $3\nu_4$, $\nu_1{+}\nu_4$, $\nu_3{+}\nu_4$, $\nu_1{+}\nu_2$, $\nu_3{+}\nu_2$), etc.

Tables I and II show further examples of resonances, the corresponding choice of N, the generating functions, and the total number of states in the polyads.

D. Explicit form of $\mathcal{N}(N)$ and its asymptotics $N \to \infty$

It is well known [8] that for the isotropic K-dimensional harmonic oscillator the number of states in the polyad N is given by a polynomial in N of degree $K{-}1$ [see Eq. (3)]. In a more complicated case $\mathcal{N}(N)$ is a polynomial of the same degree but with oscillating coefficients (see Appendix B). In other words, these coefficients are functions of $N \bmod P$. The period of oscillations P is defined by the resonance. The coefficient at the leading term (large N asymptotics) does not oscillate and its value is a characteristics of the resonance. In Appendix B we explain how to obtain explicit formulae for $\mathcal{N}(N)$ from the generating function. In the general case $\mathcal{N}(N)$ may be expressed as

TABLE II. Number of states in the polyads formed by vibratrional modes under different resonance conditions.

Resonance	$g(\lambda)$	$\mathcal{N}_{\text{regular}}(N)$	$\mathcal{N}_{\text{oscillatory}}(N)$[a]
1:1	$\frac{1}{(1-\lambda)^2}$	$N+1$	0
1:2	$\frac{1}{(1-\lambda)(1-\lambda^2)}$	$\frac{1}{2}N+\frac{3}{4}$	$\frac{1}{4}(-1)^N$
1:1:1	$\frac{1}{(1-\lambda)^3}$	$\frac{1}{2}N^2+\frac{3}{2}N+1$	0
2:1:1	$\frac{1}{(1-\lambda^2)(1-\lambda)^2}$	$\frac{1}{4}N^2+N+\frac{7}{8}$	$\frac{1}{8}(-1)^N$
5:4:4	$\frac{1}{(1-\lambda^5)(1-\lambda^4)^2}$	$\frac{1}{160}N^2+\frac{13}{160}N+\frac{15}{64}$	$\frac{1}{32}N(3-2(N\text{mod}4))\pm 1$
5:3:3	$\frac{1}{(1-\lambda^5)(1-\lambda^3)^2}$	$\frac{1}{90}N^2+\frac{11}{90}N+\frac{8}{27}$	$\frac{1}{9}N((N-1)\text{mod}3-1)\pm 1$
10:6:6:23	$\frac{1}{(1-\lambda^{10})(1-\lambda^6)^2(1-\lambda^{23})}$	$\frac{1}{368}(\frac{1}{135}N^3+\frac{1}{2}N^2+\frac{2687}{270}N+\frac{331}{6})$	$\frac{1}{1440}N^2(-1)^N+\dots$

[a] ± 1 in lines $5:4:4$ and $5:3:3$ indicates the approximate amplitude of N-independent oscillatory part, the exact values are, respectively, $\pm 291/320$ and $\pm 41/45$.

$$\mathcal{N}(N) = \mathcal{N}_{\text{regular}}(N) + \mathcal{N}_{\text{oscillatory}}(N), \tag{14}$$

where $\mathcal{N}_{\text{regular}}(N)$ is a polynomial in N of degree $K-1$ and $\mathcal{N}_{\text{oscillatory}}(N)$ is a polynomial in N with periodic coefficients. For example, in the case $K=2$ and the resonance $n_1 : n_2$ the regular part equals $\mathcal{N}_{\text{regular}}(N) = N/(n_1 n_2) + (n_1+n_2)/(2n_1 n_2)$ and the period of oscillations is $n_1 n_2$. This follows from the expansion of type (8). In the case $K=3$ and the resonance conditions $n_1 : n_2 : n_3 = 2:1:2$ [Fig. 1, right, and Eq. (2)] the period of oscillations equals two, and the amplitude of oscillations increases linearly with N. Other examples are given in Table II and Appendix B.

E. Differential and integral density of states

We can represent our results both as a function $\mathcal{N}(N)$ and $\mathcal{N}(E)$. In the harmonic approximation the energy E of the polyad N with respect to the energy of the ground state is [7]

$$E(N) - E(0) = \nu N, \tag{15}$$

where $\nu = E(N+1) - E(N)$ is the energy gap between neighboring polyads. This gap is obtained from the resonance conditions and the actual frequencies. In the examples of the $2:1:1$ and $2:2:2:2:1:1:1:1:1$ resonances in Sec. II C ν equals the lowest frequency. For the general case of the resonance $n_1 : n_2$ of the two modes ν_1, ν_2, such that $n_2\nu_1 = n_1\nu_2$, we have $\nu = \nu_1/n_1 = \nu_2/n_2$. Similarly, for the resonance $5:3:3$ in Table II $\nu \approx \nu_1/5 \approx \nu_2/3$.

The differential density of states can be obtained from $\mathcal{N}(N)$ or from $\mathcal{N}(E)$ by dividing them by ν. The integral number of states in polyads $0, 1, \dots, N$ is given by the generating function

$$g_{\text{integral}}(\lambda) = \frac{g(\lambda)}{1-\lambda}, \tag{16}$$

where $g_(\lambda)$ is the generating function for the number of states in polyads, such as (4) and (12), or the generating functions given in Table II. It is useful to note that in principle, multiplying by a factor $1/(1-\lambda)$ transforms the generating function for a differential property into the generating function for an integral property. Thus we can easily convert the differential density of states into the integral density.

III. NUMBER OF STATES OF GIVEN SYMMETRY

Consider a molecule which has K vibrational degrees of freedom and which is invariant under symmetry group G. Vibrational modes of this molecule are classified according to the irreducible representations $\{\Gamma_1, \Gamma_2, \dots, \Gamma_S\}$ of G. Some of the vibrational modes can be degenerate and then $S < K$. In other words,

$$\sum_{j=1}^{S}[\Gamma_j] = K, \tag{17}$$

where by $[\Gamma]$ we denote the dimension of representation Γ. Furthermore, depending on the problem we can consider either all or only some of the modes of the molecule. Together all the modes we consider span a (generally) reducible representation $\Gamma_{\text{initial}} = \Gamma_1 \oplus \Gamma_2 \oplus \cdots$. In the zero-order harmonic approximation the vibrational states of the molecule are described by the basis functions $|(N_1, \alpha_1), (N_2, \alpha_2), \ldots\rangle$, where N_j is the number of quanta in mode Γ_j, and α_j is a set of auxiliary quantum numbers to distinguish the excited states of mode Γ_j with the same number of quanta N_j. We want to find the number of all excited vibrational states of symmetry Γ_{final} characterized by a given distribution of quanta $\{N_1, N_2, \ldots\}$. This is a standard group-theoretical problem which may be solved using Molien generating functions [9–11,44–46]. The theory is summarized in Appendix A. In Sec. III A below we explain the main idea of this theory using the example of the triatomic molecule of symmetry D_{3h} (Table I). Further we also apply this theory to more complicated cases of AB_4 (T_d) and AB_2 ($D_{\infty h}$).

For each possible Γ_{final} we first obtain the generating function $g^{\Gamma_{\text{final}}}(\lambda_1, \lambda_2, \ldots)$ whose auxiliary variables $\lambda_1, \lambda_2, \ldots$ correspond to the modes $\Gamma_1, \Gamma_2, \ldots$ we consider. The coefficient $C_{N_1 N_2 \ldots}$ of the term $\lambda_1^{N_1}\lambda_2^{N_2}\ldots$ in the Taylor expansion of such a function gives the number of states of symmetry Γ_{final} with the distribution of quanta $\{N_1, N_2, \ldots\}$. Then, as outlined in Sec. II C, we take into account the appropriate resonance condition $n_1 : n_2 : \cdots$ and introduce one single auxiliary variable λ and the corresponding polyad quantum number N.

In all cases the main result is the set of generating functions $g^{\Gamma_{\text{final}}}(\lambda)$, such that their sum equals $g(\lambda)$, the generating function for the total number of states introduced in the previous section,

$$g(\lambda) = \sum_{\text{all }\Gamma} [\Gamma]\, g^{\Gamma}(\lambda). \tag{18}$$

If we expand each of $g^{\Gamma}(\lambda)$ in a power series similar to (5) coefficients of λ^N give $\mathcal{N}^{\Gamma}(N)$, the number of vibrational states of given symmetry Γ in the polyad N. Of course

$$\mathcal{N}(N) = \sum_{\text{all }\Gamma} [\Gamma]\, \mathcal{N}^{\Gamma}(N). \tag{19}$$

The density of states can be obtained from $\mathcal{N}^{\Gamma}(N)$ by dividing the latter by $\nu = E(N) - E(N{+}1)$, the energy gap between the neighboring polyads. Along with the number of states $\mathcal{N}^{\Gamma}(N)$ and the corresponding density of states it is often useful to consider the partial density

$$\mathcal{N}^{\Gamma}_{\text{partial}}(N) = \frac{\mathcal{N}^{\Gamma}(N)}{\mathcal{N}(N)}. \tag{20}$$

The large-N asymptotic behavior of the partial density (20) is defined completely by the symmetry group [47]: at large N the ratio of partial densities of states equals the ratio of the squares of the dimensions of the corresponding representations,

$$\lim_{N\to\infty} \frac{\mathcal{N}^{\Gamma_k}_{\text{partial}}(N)}{\mathcal{N}^{\Gamma_i}_{\text{partial}}(N)} = \frac{[\Gamma_k]^2}{[\Gamma_i]^2}. \tag{21}$$

This was formulated as a general conjecture in Refs. [16–18]. A constructive proof of (21) can be given if for each finite group G and Γ_{initial} we take generating functions $g^{\Gamma}(\lambda)$ for all possible irreducible representations Γ of G (see Appendix A and Ref. [48]) and transform them into explicit expressions for $\mathcal{N}^{\Gamma}(N)$ (Appendix B). In the limit $N \to \infty$ we leave only the terms of highest degree in N. These terms do not oscillate and have the same degree for each final representation Γ.

A. Vibrational polyads of A_3 (D_{3h})

A triatomic molecule A_3 with the equilibrium configuration of symmetry $G = D_{3h}$ has one nondegenerate vibrational mode $\nu_1(A_1')$ and one double degenerate mode $\nu_2(E')$ (see Table I). Since all vibrations occur in the plane, both ν_1 and ν_2 are σ_h-invariant. As a result, all vibrational states are also σ_h-invariant. The image [47] of D_{3h} in the representation $A_1' \oplus E'$ is C_{3v}, and below we simply use the C_{3v} notation for irreducible representations (without primes).

First we consider the two modes independently. Thus, if $\Gamma_{\text{initial}} = A_1$ only totally symmetric states can be constructed, i.e., $\Gamma_{\text{final}} \equiv A_1$. The generating function for the total number of states with N_1 quanta of ν_1 is trivial [cf. Eqs. (A12) and (4)]

$$g(\Gamma_{\text{final}}{=}A_1, \Gamma_{\text{initial}}{=}A_1; \lambda_1) = \frac{1}{1-\lambda_1}. \tag{22}$$

On the other hand, if $\Gamma_{\text{initial}} = E$ we can construct vibrational states of symmetry $\Gamma_{\text{final}} = A_1$, A_2, and E. The corresponding generating functions $g(\Gamma_{\text{final}}, \Gamma_{\text{initial}}{=}E; \lambda_2)$ are given in Eqs. (A15) [48].

Now we consider the two modes together, i.e., $\Gamma_{\text{initial}} = A_1 \oplus E$. We use auxiliary variables λ_1 and λ_2 and obtain a two parameter generating function for the total number of states of symmetry Γ_{final} with N_1 quanta in mode ν_1 and N_2 quanta in mode ν_2 [Sec. II B, Eq. (9a)],

$$g(A_1; A_1 \oplus E; \lambda_1, \lambda_2) = \frac{1}{(1-\lambda_1)(1-\lambda_2^2)(1-\lambda_2^3)}, \tag{23a}$$

$$g(A_2; A_1 \oplus E; \lambda_1, \lambda_2) = \frac{\lambda_2^3}{(1-\lambda_1)(1-\lambda_2^2)(1-\lambda_2^3)}, \tag{23b}$$

$$g(E; A_1 \oplus E; \lambda_1, \lambda_2) = \frac{\lambda_2 + \lambda_2^2}{(1-\lambda_1)(1-\lambda_2^2)(1-\lambda_2^3)}. \tag{23c}$$

[Possible Γ_{final} are again A_1, A_2, and E. Since $A_1 \times \Gamma = \Gamma$ for all Γ, the total generating function $g(\Gamma; A_1 \oplus E; \lambda_1, \lambda_2)$ in (23) is just a product of (22) and $g^{C_{3v}}(\Gamma; E; \lambda_2)$ in (A15).]

If the molecule A_3 is characterized by the resonance $\nu_1 : \nu_2 \approx n_1 : n_2$ we transform the two-parameter generating functions (23) into one-parameter functions by substitution $\lambda_1 = \lambda^{n_1}$ and $\lambda_2 = \lambda^{n_2}$ (Secs. II C and IV A). This is done in Sec. IV D on the example of H_3^+.

B. Vibrational polyads of AB_4 (T_d)

The total number of states $\mathcal{N}(N)$ in the polyads formed by four stretching and five bending vibrations of a tetrahedral molecule, such as CH_4 in Table I, follows from the generating function in Eqs. (12) and (13),

$$\begin{aligned} \mathcal{N}(N) = 24\mathcal{N}_{\text{lead}}(N) &+ \frac{1}{2^8}\left(\frac{563}{15}N^4 + \frac{28457}{180}N^3 + \frac{970241}{2520}N^2 + \frac{204347}{420}N + \frac{3797}{16}\right) \\ &+ \frac{(-1)^N}{2^{10}}\left(\frac{1}{3}N^3 + \frac{13}{2}N^2 + \frac{119}{3}N + \frac{299}{4}\right) , \end{aligned} \tag{24}$$

with the leading term

$$\mathcal{N}_{\text{lead}}(N) = \frac{1}{2^{12}\cdot 5}\left(\frac{N^8}{4\cdot 27\cdot 7} + \frac{13N^7}{27\cdot 7} + \frac{3N^6}{2} + \frac{13\cdot 37\, N^5}{27}\right) . \tag{25}$$

To convert the generating function (12) into the explicit formulae (24) and (25) for the number of states we can either use an algebraic transformation of the generating function into the sum of elementary fractions (Appendix B and Ref. [49]), or reconstruct the polynomial from its values, i.e., the known numbers of states for $N = 0, 1, 2, \ldots, N_{\text{max}}$.

To construct the generating function for the number of states of symmetry $\Gamma_{\text{final}} = A_1, A_2, E, F_1, F_2$, we use the method in Appendix A. Essentially we follow the same procedure as in Sec. III A. In this case $\Gamma_{\text{initial}} = A_1 \oplus E \oplus F_2 \oplus F_2$. Generating functions for individual irreducible representations [48] in Γ_{initial} are given in Eqs. (A12), (A15), and Table IV. These functions should be combined according to Eq. (A8) as explained in Appendix A 1. Then we substitute $\lambda_1, \lambda_3, \lambda_2, \lambda_4$ for one auxiliary variable λ using the resonance condition $2:2:1:1 \approx \nu_1 : \nu_3 : \nu_2 : \nu_4$ [cf. Eqs. (12) and (13)]. This results in a set of functions $g^{\Gamma_{\text{final}}}(\lambda)$ [50]

$$g^{A_1} = \frac{2\,\lambda^{14} - 2\,\lambda^{13} + 5\,\lambda^{12} + 2\,\lambda^{10} + \lambda^9 + 5\,\lambda^8 + 2\,\lambda^6 + 2\,\lambda^4 + 2\,\lambda^2 - 2\,\lambda + 1}{(1-\lambda)^2\,(1-\lambda^2)^2\,(1-\lambda^3)^2\,(1-\lambda^4)(1-\lambda^6)(1-\lambda^8)}, \tag{26a}$$

$$g^{A_2} = \frac{\lambda^3(\lambda^{14} - 2\,\lambda^{13} + 2\,\lambda^{12} + 2\,\lambda^{10} + 2\,\lambda^8 + 5\,\lambda^6 + \lambda^5 + 2\,\lambda^4 + 5\,\lambda^2 - 2\,\lambda + 2)}{(1-\lambda)^2\,(1-\lambda^2)^2\,(1-\lambda^3)^2\,(1-\lambda^4)(1-\lambda^6)(1-\lambda^8)}, \tag{26b}$$

$$g^E = \frac{\lambda(\lambda^{10} - \lambda^9 + \lambda^8 + 3\,\lambda^7 - 3\,\lambda^6 + 7\,\lambda^5 - 3\,\lambda^4 + 3\,\lambda^3 + \lambda^2 - \lambda + 1)}{(1-\lambda)^3\,(1-\lambda^2)(1-\lambda^3)^2\,(1-\lambda^4)^2\,(1-\lambda^6)}, \tag{26c}$$

$$g^{F_1} = \frac{\lambda^2(\lambda^6 - \lambda^5 - \lambda^4 + 5\,\lambda^3 - 4\,\lambda^2 + \lambda + 1)}{(1-\lambda)^4\,(1-\lambda^2)^3\,(1-\lambda^4)(1-\lambda^8)}, \tag{26d}$$

$$g^{F_2} = \frac{\lambda(\lambda^6 + \lambda^5 - 4\,\lambda^4 + 5\,\lambda^3 - \lambda^2 - \lambda + 1)}{(1-\lambda)^4\,(1-\lambda^2)^3\,(1-\lambda^4)(1-\lambda^8)}. \tag{26e}$$

Using the method of Appendix B we convert functions (26) into the number-of-states polynomials $\mathcal{N}^\Gamma(N)$,

$$\mathcal{N}^{A_1}(N) = \mathcal{N}_{\text{lead}}(N) + \frac{1}{2^9\cdot 45}\left(\frac{3\,N^5}{4} + 167N^4 + \frac{7\cdot 59\cdot 109\,N^3}{48}\right) + \frac{(-1)^N}{2^{12}\cdot 3}\left(N^4 + \frac{13^2\,N^3}{6}\right) + O(N^2)\ , \tag{27a}$$

$$\mathcal{N}^{A_2}(N) = \mathcal{N}_{\text{lead}}(N) - \frac{1}{2^9\cdot 45}\left(\frac{3N^5}{4} - \frac{473\,N^4}{4} - \frac{11^2\cdot 137\,N^3}{48}\right) - \frac{(-1)^N}{2^{12}\cdot 3}\left(N^4 + \frac{143\,N^3}{6}\right) + O(N^2), \tag{27b}$$

$$\mathcal{N}^{E}(N) = 2\mathcal{N}_{\text{lead}}(N) + \frac{1}{2^{11}\cdot 45}\left(7\cdot 167\,N^4 + \frac{13\cdot 23\cdot 103\,N^3}{6}\right) + (-1)^N\frac{13N^3}{2^{12}\cdot 9} + O(N^2)\ , \tag{27c}$$

$$\mathcal{N}^{F_1}(N) = 3\mathcal{N}_{\text{lead}}(N) + \frac{1}{2^7}\left(-\frac{95\,N^5}{48} + \frac{11N^4}{5} + \frac{22937N^3}{2^6\cdot 45}\right) - \frac{(-1)^N}{2^{12}\cdot 3}\left(N^4 + \frac{55\,N^3}{2}\right) + O(N^2)\ , \tag{27d}$$

$$\mathcal{N}^{F_2}(N) = 3\mathcal{N}_{\text{lead}}(N) + \frac{1}{2^{11}\cdot 15}\left(N^5 + 593N^4 + \frac{77\cdot 421\,N^3}{12}\right) + \frac{(-1)^N}{2^{12}\cdot 3}\left(N^4 + \frac{49N^3}{2}\right) + O(N^2)\ . \tag{27e}$$

It is straightforward to verify that

$$g^{A_1} + g^{A_2} + 2g^E + 3g^{F_1} + 3g^{F_2} = g_{\text{total}} = \frac{1}{(1-\lambda)^5(1-\lambda^2)^4}. \tag{28}$$

Correspondingly, the asymptotic relation between the numbers of states of different symmetry

$$\mathcal{N}_{\text{total}}(N) = \sum_\Gamma [\Gamma]\mathcal{N}^\Gamma(N) = \frac{24}{[\Gamma]}\mathcal{N}^\Gamma(N) + O(N^5) \tag{29}$$

holds up to the terms of order N^{-3} with respect to the leading term of the asymptotic expansion.

The numbers of states obtained from functions (26) are given in Table III. Figure 2 shows the partial differential density (20) as a function of polyad quantum number N. For example, for $N = 2$ we see that 3/19, 3/19, 4/19, and 9/19 of all states are, respectively, of type $\Gamma = A_1$, F_1, E, and F_2. (Use the degeneracy $[\Gamma]$ when counting states.) We also see from the graphics that, at high N, the functions $\mathcal{N}^\Gamma_{\text{partial}}(N)$ reach the asymptotic values 1/24 for representations A_1 and A_2 ($[A] = 1$), $4/24 = 1/6$ for E ($[E] = 2$), and $9/24 = 3/8$ for F_1 and F_2 ($[F] = 3$).

C. Vibrational polyads of linear molecule AB_2 ($D_{\infty h}$)

Vibrational modes of the AB_2 ($D_{\infty h}$) molecule span a four dimensional reducible representation $\Sigma_g^+ + \Sigma_u^+ + \Pi_u$. The three parameter generating function $g(\Gamma; \Sigma_g^+ + \Sigma_u^+ + \Pi_u; \lambda_1, \lambda_2, \lambda_3) = g(\Gamma)$ for the number of tensors of symmetry Γ constructed from powers of $\Sigma_g^+ + \Sigma_u^+ + \Pi_u$ can be easily found by combining the generating functions (A11) for the initial irreducible representations (see Table VII of Appendix A). The variable λ_i describes excitations of mode i.

$$g(\Sigma_g^+) = \frac{1}{(1-\lambda_1)\,(1-\lambda_2^2)\,(1-\lambda_3^2)}, \tag{30a}$$

$$g(\Sigma_u^+) = \frac{\lambda_3}{(1-\lambda_1)\,(1-\lambda_2^2)\,(1-\lambda_3^2)}, \tag{30b}$$

$$g(E_{2k}^g) = \frac{(\lambda_2)^{2k}}{(1-\lambda_1)\,(1-\lambda_2^2)\,(1-\lambda_3^2)}, \tag{30c}$$

$$g(E_{2k}^u) = \frac{\lambda_3\,(\lambda_2)^{2k}}{(1-\lambda_1)\,(1-\lambda_2^2)\,(1-\lambda_3^2)}, \tag{30d}$$

TABLE III. Decomposition of vibrational polyads for the AB_4 (T_d) molecule into irreducible symmetry species.

N	A_1	A_2	E	F_1	F_2	$\mathcal{N}(N)$[a]
0	1	0	0	0	0	1
1	0	0	1	0	1	5
2	3	0	2	1	3	19
3	4	2	5	5	8	55
4	11	2	14	13	20	140
5	18	11	28	34	43	316
6	41	20	58	71	90	660
7	64	45	112	148	169	1284
8	126	81	204	272	313	2370
9	199	158	354	495	540	4170
10	342	257	602	836	917	7062
11	529	448	974	1395	1480	11550
12	852	701	1547	2211	2356	18348
13	1263	1118	2387	3462	3613	28380
14	1930	1679	3603	5225	5470	42900
15	2785	2540	5319	7796	8047	63492
16	4063	3663	7732	11312	11703	92235

[a]The total number of states within polyad N. The degeneracy of states is taken into account as in Eqs. (19) and (28).

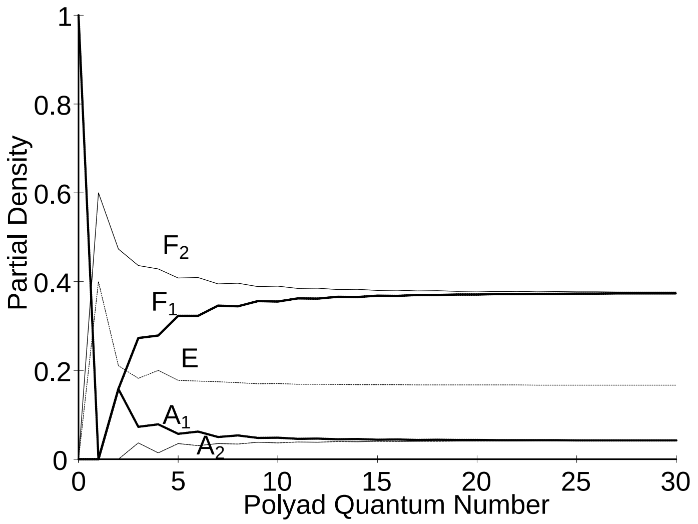

FIG. 2. Partial numbers of vibrational states of different symmetry types versus the polyad quantum number defined in (26-26e) for tetrahedral molecules AB_4.

$$g(E^u_{2k+1}) = \frac{(\lambda_2)^{2k+1}}{(1-\lambda_1)\,(1-\lambda_2^2)\,(1-\lambda_3^2)}, \tag{30e}$$

$$g(E^g_{2k+1}) = \frac{\lambda_3\,(\lambda_2)^{2k+1}}{(1-\lambda_1)\,(1-\lambda_2^2)\,(1-\lambda_3^2)}. \tag{30f}$$

It is straightforward to verify that

$$g(\Sigma_g^+) + g(\Sigma_u^+) + 2\sum_{k=1}^{\infty}(g(E_k^g) + g(E_k^u)) = \frac{1}{(1-\lambda_1)(1-\lambda_2)^2(1-\lambda_3)}. \tag{31}$$

To apply the generating functions (30) to concrete $D_{\infty h}$ molecules, such as CS_2 in Table I, we take into account the resonance conditions of type $n_1 : n_2 : n_2 : n_3$ and replace λ_1 by λ^{n_1}, λ_2 by λ^{n_2}, and λ_3 by λ^{n_3}. For CS_2 these resonance conditions may be taken in the form $10 : 6 : 6 : 23$ which corresponds to the following relation between the harmonic frequencies $69\nu_1 \sim 115\nu_2 \sim 30\nu_3$ [51,52]. Figure 3 shows that for linear molecules more new symmetry

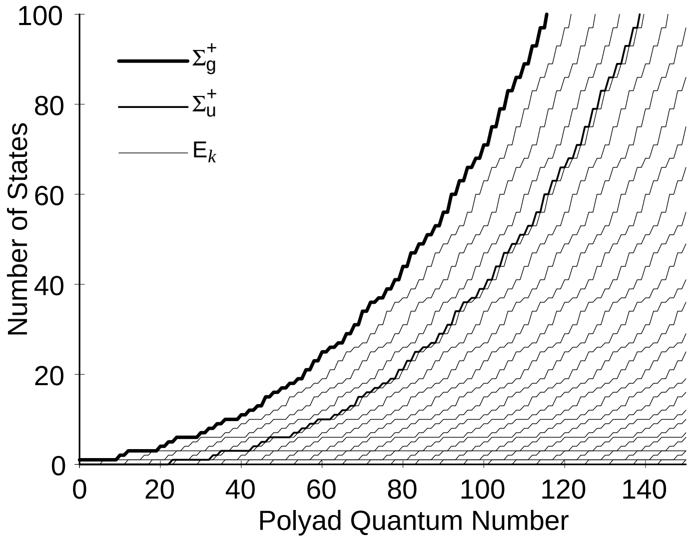

FIG. 3. Partial differential density of vibrational states of different symmetry types versus energy for the linear molecule CS_2.

types arise with increasing energy (or the polyad quantum number). This is due to the infinite number of different irreducible representation for the $D_{\infty h}$ group.

IV. GENERALIZATIONS.

A. Arbitrary resonance. Harmonic model.

The most general resonance condition between K vibrational modes can be always represented in the form

$$\nu_1 : \nu_2 : \nu_3 : \cdots : \nu_K = n_1 : n_2 : n_3 : \cdots : n_K . \tag{32}$$

the numbers n_i are integers and several n_i can equal each other. Each of the frequencies ν_i can be expressed as $n_i \nu$, where ν is the small auxiliary quantum introduced in Sec. II E.

The corresponding polyad quantum number is

$$N = n_1 N_1 + n_2 N_2 + \ldots + n_K N_K . \tag{33}$$

Expression (33) defines N as an integer. Alternative definitions of the polyad quantum number are possible. We can define the polyad quantum number in terms of quantum ν_α, so that $N_\alpha = N/n_\alpha$. For example, we can choose the mode α as the most intense mode of the IR spectrum. Then the polyad with integer N_α contains the overtone $N_\alpha \nu_\alpha$. Such overtones show up as the strongest lines in the spectrum of the transition between the ground state and the polyad N_α. Such mode-dependent polyad number definition correlates with the standard spectroscopic notation of overtones. We, however, prefer to work with an integer polyad quantum number (33).

The generating function for the number of states within a polyad characterized by the quantum number N in Eq. (33) has the form

$$g_{n_1:n_2:\cdots:n_K}(\lambda) = \prod_{s=1}^{K} (1 - \lambda^{n_s})^{-1} . \tag{34}$$

The corresponding leading asymptotic term for $\mathcal{N}(N)$ is

$$\mathcal{N}(N) \propto \frac{N^{K-1}}{(n_1 n_2 \cdots n_k)(K-1)!} . \tag{35}$$

The period of $\mathcal{N}_{\mathrm{oscillatory}}(N)$ is given by the least common multiple $P = \mathrm{lcm}(n_1, n_2, \ldots, n_K)$.

B. Number of rotational states

The total number of the rotational states in the rotational multiplet characterized by the total angular momentum quantum number J is given by the generating function

$$g_{\rm rot}(\mu) = \frac{1+\mu}{(1-\mu)^2} = 1 + 3\mu + 5\mu^2 + \ldots + (2J+1)\mu^J + \ldots . \tag{36}$$

[We consider only $(2J+1)$ rotational levels in the rotational multiplet and neglect the additional $(2J+1)$ degeneracy due to the isotropy of the physical space.]

In the presence of symmetry this rotational multiplet decomposes into the states of several different symmetry types Γ. To obtain the generating function for the rotational states of each symmetry type we follow Appendix A. Such states are built from three rotational functions $|J=1,M\rangle$. Therefore, this problem is equivalent to constructing rotational tensors from powers of (J_x, J_y, J_z), which are restricted on

$$\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2 = J(J+1) = \text{const.} \tag{37}$$

For example, in the case of the T_d group components (J_x, J_y, J_z) of the elementary rotational tensor span the three-dimensional representation F_1. We obtain the required generating functions from Table IV using $\Gamma_i = F_1$. To account for (37) we should remove factor $(1-\lambda^2)$ from the denominator, since this factor distinguishes tensors that differ by power of $\mathbf{J}^2$. The resulting generating functions are

$$g_{\rm rot}^{A_1}(\mu) = \frac{1+\mu^9}{(1-\mu^4)(1-\mu^6)}, \tag{38a}$$

$$g_{\rm rot}^{A_2}(\mu) = \frac{\mu^3+\mu^6}{(1-\mu^4)(1-\mu^6)}, \tag{38b}$$

$$g_{\rm rot}^{E}(\mu) = \frac{\mu^2+\mu^4+\mu^5+\mu^7}{(1-\mu^4)(1-\mu^6)}, \tag{38c}$$

$$g_{\rm rot}^{F_1}(\mu) = \frac{\mu+\mu^3+\mu^4+\mu^5+\mu^6+\mu^8}{(1-\mu^4)(1-\mu^6)}, \tag{38d}$$

$$g_{\rm rot}^{F_2}(\mu) = \frac{\mu^2+\mu^3+\mu^4+\mu^5+\mu^6+\mu^7}{(1-\mu^4)(1-\mu^6)}. \tag{38e}$$

C. Number of rotation-vibration states

Another important generalization concerns the calculation of all rovibrational levels with given rotational quantum number J and polyad number N. The total number of such states is given by the two parameter generating function, such as in (7). Namely from (36) and (34) we obtain

$$g_{\rm vib-rot}^{\rm total}(\lambda,\mu) = \frac{1+\mu}{(1-\mu)^2}\prod_{s=1}^{K}(1-\lambda^{n_s})^{-1}. \tag{39}$$

Generating functions for each symmetry type are obtained from $g_{\rm rot}^{\Gamma_1}(\mu)$ and $g_{\rm vib}^{\Gamma_2}(\lambda)$ according to (A11). For example, if we consider a molecule of symmetry T_d the generating function for the number of the rovibrational states of type A_1 has the form

$$g_{\rm vib-rot}^{A_1}(\lambda,\mu) = \sum_{\text{all }\Gamma} g_{\rm vib}^{\Gamma}(\lambda) g_{\rm rot}^{\Gamma}(\mu). \tag{40}$$

The expansion of the generating function in a power series in λ and μ yields

$$g_{vib-rot}^{\Gamma}(\lambda,\mu) = \sum_{N,J} c_{NJ}^{\Gamma}\lambda^N\mu^J, \tag{41}$$

where the coefficient c_{NJ}^{Γ} gives the number of states of the symmetry type Γ in the vibrational polyad N and with the rotational quantum number J.

Figure 4 illustrates partial densities of rovibrational states as a function of rotational quantum number for several polyads. It shows clearly that for higher polyads the asymptotic distribution for different symmetry types is reached for lower J values.

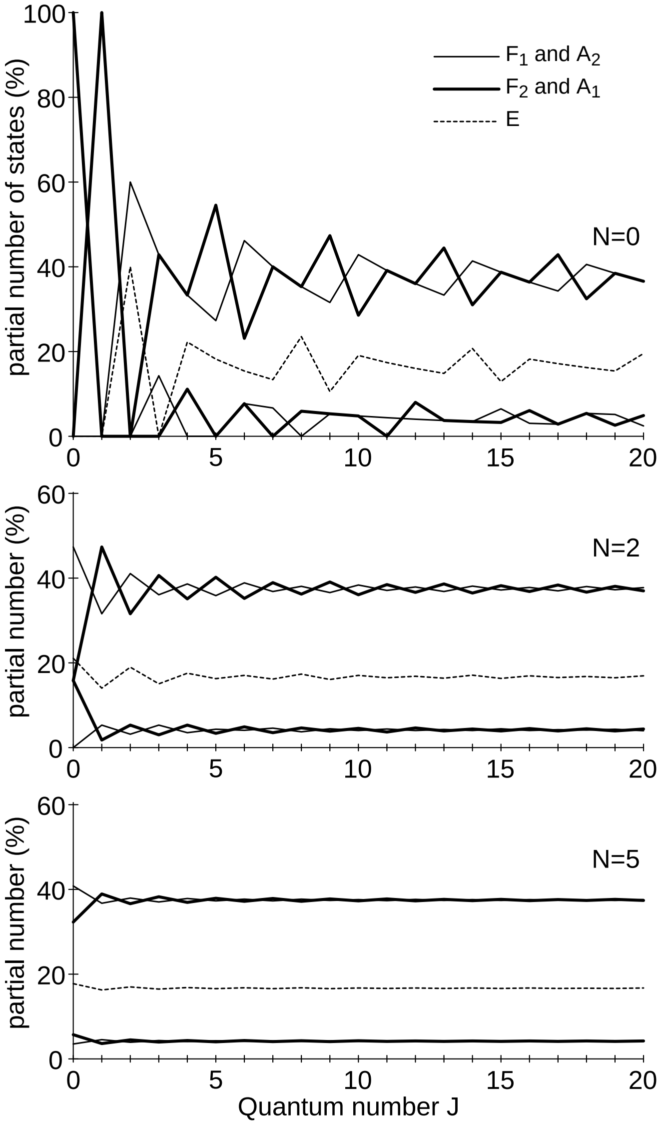

FIG. 4. Partial numbers of rovibrational states of different symmetry types versus rotational quantum number J for the vibrational polyads of tetrahedral molecules AB_4.

D. Anharmonic model

The calculation in the harmonic approximation assumes the linear relation (15) between the polyad quantum number N and the vibrational energy $E_{\rm vib}$. We can easily introduce a phenomenological nonlinear (in N) correction to the vibrational energy which partially accounts for the anharmonicity, namely for the anharmonicity associated with the polyad quantum number [6]. To demonstrate the reliability of such approach we calculate partial densities of states for the H_3^+ molecular ion for which all vibrational states are known with relatively high accuracy from the direct *ab initio* calculations [53,54].

We use the resonance condition 5:4:4 ($5\nu_1 \approx 4\nu_2$) between the nondegenerate mode ν_1 and the doubly degenerate mode ν_2 and introduce the polyad quantum number

$$N = 5N_1 + 4N_2, \tag{42}$$

with N_1 and N_2 being the numbers of quanta in modes ν_1 and ν_2. (N gives the number of auxiliary quanta distributed between the two modes in resonance. For H_3^+ the auxiliary frequency $\nu = 632.9925\ \mathrm{cm}^{-1}$.)

Generating functions for the differential density of states follow from (23) with $\lambda_1 = \lambda^5$ and $\lambda_2 = \lambda^4$,

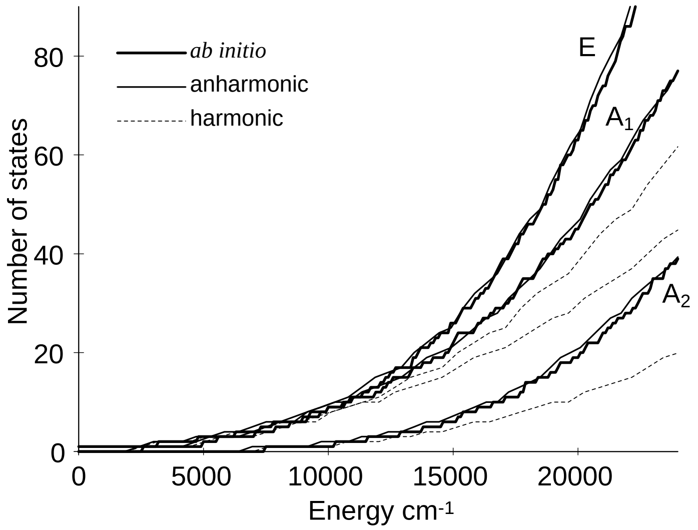

FIG. 5. Integral densities of vibrational states of different symmetry types versus energy for the H_3^+ ion. Densities in the harmonic approximation, anharmonicity corrected densities, and *ab initio* densities by Tennyson *et al* [54] are shown. For the symmetry type E we count the number of double degenerate states.

$$g(A_1; A_1{+}E; \lambda) = \frac{1}{(1-\lambda^5)(1-\lambda^8)(1-\lambda^{12})}, \tag{43a}$$

$$g(A_2; A_1{+}E; \lambda) = \frac{\lambda^{12}}{(1-\lambda^5)(1-\lambda^8)(1-\lambda^{12})}, \tag{43b}$$

$$g(E; A_1{+}E; \lambda) = \frac{\lambda^4+\lambda^8}{(1-\lambda^5)(1-\lambda^8)(1-\lambda^{12})}. \tag{43c}$$

The integral density is described by (43) and (16). As a function of energy this density can be easily compared with that obtained from the *ab initio* calculations. Figure 5 shows that at high energy the *ab initio* integral density differs significantly from that calculated on the base of (43). This discrepancy is not surprising because the harmonic approximation used in (43) is certainly insufficient. To have a better agreement we make a nonlinear transformation [7]

$$E(N) = N\nu_0\,(1 + \sum_{i=1} a_i N^i), \tag{44}$$

and find coefficients a_i that fit the integral density of the A_1 states of the direct quantum calculations. The *same* coefficients correct the integral densities of the A_2 and E states. Figure 5 shows unambiguously that integral densities for the A_2 and E vibrational states are reproduced with high accuracy, even though no polyad splitting has been introduced. Numerical values of coefficients a_i indicate that the nonlinear transformation (44) has good convergence properties. (Coefficients a_i decrease rapidly: $a_1 = -1.40546\ 10^{-2}$, $a_2 = 0.8482\ 10^{-3}$, $a_3 = 2.52\ 10^{-5}$, $a_4 = 2\ 10^{-7}$). This indicates that the coefficients in (44) may be explained by reducing the initial vibrational Hamiltonian of H_3^+ to its normal form with respect to the approximate integral of motion corresponding to the polyad quantum number [6].

Figure 5 does not show clearly if the asymptotic ratio of different symmetry type levels is achieved in the case of H_3^+. Figure 6 is more helpful in this regard: it shows that for $E \approx 24\,000$ cm^{-1} the theoretical limit defined by Eq. (21) for the partial integral densities as $D(A_1) : D(A_2) : D(E) = 1 : 1 : 4$ is not yet achieved but is qualitatively correct. Note that our description not only gives the proper high energy limit of partial densities but also reproduces them well at all intermediate energies.

V. CONCLUSIONS

The main idea of the present work was to derive simple exact analytical formulae for the numbers and the density of states of a system of coupled quantum oscillators using, initially, a purely harmonic model. We wanted to understand if and how such formulae could be applied to realistic problems, such as the vibrational structure of polyatomic molecules.

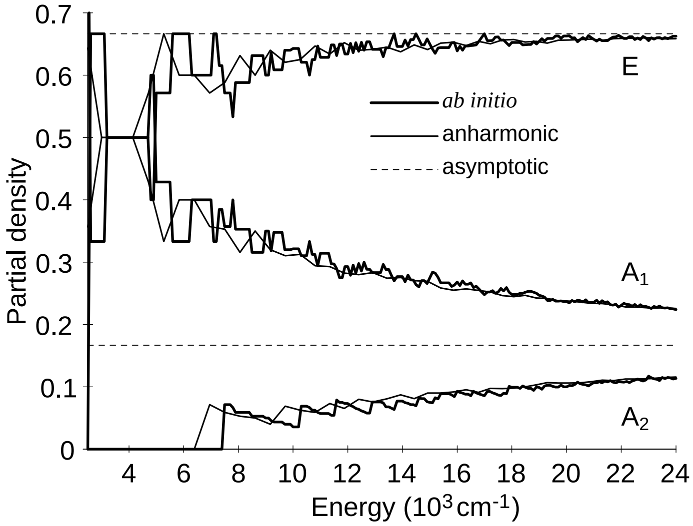

FIG. 6. Partial integral densities of vibrational states of different symmetry types versus energy for the H_3^+ ion. Anharmonicity corrected densities, and *ab initio* densities calculated by Tennyson *et al* [54] are given. For the E states we take into account their degeneracy.

Our purpose has indeed been achieved. The example of H_3^+ in Sec. IV D shows that after a modest phenomenological correction our formulae do reproduce the actual densities of states. The results are not only qualitatively correct but can also be used in quantitative studies.

The advantage of our approach is due to the simplicity of the required calculations. It allows for a quick and reliable estimate by a non-specialist, and requires the absolute minimum of the information on the system. Furthermore, given the small number of phenomenological parameters, the approach presented can easily be used to analyze experimental data and to extract in this way the characteristics of the nonlinearity of the system. This is contrary to extensive quantum variational or semiclassical calculations which are undoubtedly more correct but require large amounts of data on the potential, ample computer time, and which are, in fact, the matter of specialized state-of-the-art research.

Despite the evident success we should stress that the validity of the approach, as well as the physical meaning of the as yet phenomenological parameters, needs further investigation.

ACKNOWLEDGMENTS

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APPENDIX A: MOLIEN FUNCTIONS

This appendix summarizes some results of the classical theory of invariants necessary to compute the Molien generating functions for the numbers of invariants and covariants. The main mathematical tool is the Molien function introduced at the end of the 19-th century [9]. Mathematical ideas were developed mainly at the beginning of our century [10,11,44–46]. Physical applications of this technique were done only during the last 20 years [26,38,39,27–29,35,31,36,37,32–34,30].

Let $\{t_\alpha^{\Gamma_0}\}$, $(\alpha = 1, 2, \ldots, [\Gamma_0])$ be an elementary tensor of symmetry type Γ_0 with respect to the initial symmetry group G. We suppose that G is a point symmetry group. We also suppose that all components of tensor operators commute with each other. Let us use $\{t_\alpha^{\Gamma_0}\}$ to construct the set of all tensors of degree Ω with respect to $t_\alpha^{\Gamma_0}$. This set of tensor operators forms the basis of a (generally) reducible representation of the symmetry group G. To calculate the number of linearly independent operators of given symmetry type Γ and degree Ω we can use the statement known as Molien's theorem.

Statement 1 (Molien theorem) Expression

$$g(\lambda) = \frac{1}{[G]} \sum_p \frac{h_p \chi_p^{(\Gamma)*}}{\det(E - \lambda X_p^{(\Gamma_0)})} \tag{A1}$$

is the generating function for the number of linearly independent operators of degree Ω and symmetry type Γ, which can be constructed from elementary tensors t^{Γ_0}. In (A1) λ is an auxiliary variable; $[G]$ is the order (the number of elements) of group G; h_p is the number of elements within the class of conjugate elements; $\sum_p$ is the sum over classes of conjugated elements; χ_p^{Γ} is the character of irreducible representation Γ for class p; $X_p^{\Gamma_0}$ is the matrix of the representation Γ_0 for an element from class p (the dimension of this matrix equals the dimension of the representation Γ_0); E is the identity matrix of the same dimension; $\det(E - \lambda X_p^{(\Gamma_0)})$ is the characteristic polynomial for matrix $X_p^{\Gamma_0}$. (Characteristic polynomial does not depend on which symmetry element is chosen from the given class of conjugated elements.)

The notion "*generating function*" introduced in the Molien theorem means that after the expansion of $g(\lambda)$ into a formal power series in the auxiliary variable λ

$$g(\lambda) = \sum_{\Omega} C_{\Omega} \lambda^{\Omega} \tag{A2}$$

the coefficient C_{Ω} equals the number of linearly independent tensors of degree Ω and symmetry type Γ.

Calculation of the characteristic polynomial in (A1) can be done without using the explicit matrix representation for $X_p^{\Gamma_0}$. Two next statements show that one can use either the eigenvalues of the representation matrix, or even simply its characters.

Statement 2 Let the decomposition of Γ_0 into irreducible representations be $\Gamma_0 = \Gamma_1 + \Gamma_2 + \ldots + \Gamma_k$. Then the characteristic polynomial

$$\begin{aligned} \det(E - \lambda X_p^{(\Gamma_0)}) &= \det(E - \lambda X_p^{(\Gamma_1)}) \det(E - \lambda X_p^{(\Gamma_2)}) \cdots \det(E - \lambda X_p^{(\Gamma_k)}) \\ &= [1 - \lambda \exp(i\omega_1^{(p)})] \cdots [1 - \lambda \exp(i\omega_{[\Gamma_0]}^{(p)})] \end{aligned} \tag{A3}$$

can be written in a form of product of polynomials for irreducible components of the decomposition. Further transformation leads to the representation of the characteristic polynomial as the product of factors $[1 - \lambda \exp(i\omega_q^{(p)})]$ depending on eigenvalues $\exp(i\omega_q^{(p)})$ of the matrix $X_p^{(\Gamma_0)}$.

Statement 3 The characteristic polynomial can be expressed in terms of characters,

$$\det(E - \lambda X_p^{(\Gamma_0)}) = 1 - \chi_p^{(A^1)}\lambda + \chi_p^{(A^2)}\lambda^2 - \ldots + (-1)^k \chi_p^{(A^k)}\lambda^k + \ldots + (-1)^{[\Gamma_0]}\chi_p^{(A^{[\Gamma_0]})}\lambda^{[\Gamma_0]} \, , \tag{A4}$$

where A^k denotes the k-th antisymmetric power of the representation Γ_0,

$$A^1 = \Gamma_0, \tag{A5a}$$
$$A^2 = \Gamma_0 \otimes [1^2], \tag{A5b}$$
$$A^3 = \Gamma_0 \otimes [1^3], \tag{A5c}$$
$$\ldots \quad \ldots\ \ldots$$
$$A^k = \Gamma_0 \otimes [1^k]. \tag{A5d}$$

Notation $\Gamma \otimes [1^k]$ uses the fact that the antisymmetric power of representation Γ can be considered as a pletism of representation Γ and the antisymmetric representation $[1^k]$ of the symmetric group σ_k. Explicit expressions for characters of the antisymmetric powers of representation Γ are well known for arbitrary k [55]. We list below the formulae for $k \leq 5$. (The maximum dimension of irreducible representations of any three-dimensional point group is five.)

$$\chi^{(\Gamma \otimes 1^2)}(R) = \frac{1}{2}[\chi(R)]^2 - \frac{1}{2}\chi(R^2) \tag{A6a}$$

$$\chi^{(\Gamma \otimes 1^3)}(R) = \frac{1}{6}[\chi(R)]^3 - \frac{1}{2}\chi(R)\chi(R^2) + \frac{1}{3}\chi(R^3), \tag{A6b}$$

$$\chi^{(\Gamma \otimes 1^4)}(R) = \frac{1}{24}[\chi(R)]^4 - \frac{1}{4}[\chi(R)]^2\chi(R^2) + \frac{1}{8}[\chi(R^2)]^2 - \frac{1}{4}\chi(R^4), \tag{A6c}$$

$$\begin{aligned} \chi^{(\Gamma \otimes 1^5)}(R) = {} & \frac{1}{120}[\chi(R)]^5 - \frac{1}{12}[\chi(R)]^3\chi(R^2) + \frac{1}{6}[\chi(R)]^2\chi(R^3) \\ & - \frac{1}{4}\chi(R)\chi(R^4) + \frac{1}{8}\chi(R)[\chi(R^2)]^2 - \frac{1}{6}\chi(R^2)\chi(R^3) + \frac{1}{5}\chi(R^5). \end{aligned} \tag{A6d}$$

Formulae (A4) and (A6) enable one to calculate the characteristic polynomial in terms of characters of irreducible representations. When using (A6) one should remember that the symmetry element R and its powers R^k can belong to different classes of conjugated elements.

The generating function (A1) not only gives the numbers of linearly independent terms for each degree Ω [Eq. (A2)] but also is extremely important for the construction of so-called integrity bases [11,44,45,38,50,31].

Several useful formulae are given below to allow the manipulations with generating functions and to construct more complicated functions from simpler functions and simpler groups.

Consider the detailed notation $g^G(\Gamma_f;\ \Gamma_i;\lambda)$ for the generating function (A1) with λ an auxiliary variable, Γ_i the representation spanned by initial tensors, Γ_f the representation of the resulting tensors, and G the symmetry group. If Γ_f is the totally symmetric representation, the resulting tensors are called *invariants*. Not totally symmetric tensors are usually called *covariants*.

If the final representation Γ_f can be decomposed into the sum $\Gamma_f = \Gamma_1 \oplus \Gamma_2$, the corresponding generating function has the form

$$g^G(\Gamma_1 \oplus \Gamma_2; \Gamma_i; \lambda) = g^G(\Gamma_1; \Gamma_i; \lambda) + g^G(\Gamma_2; \Gamma_i; \lambda). \tag{A7}$$

If the initial representation Γ_i decomposes as $\Gamma_i = \Gamma_{i_1} \oplus \Gamma_{i_2}$ we have

$$g^G(\Gamma_f; \Gamma_{i_1} \oplus \Gamma_{i_2}; \lambda) = \sum_{\Gamma_{f_1},\Gamma_{f_1}} n^{\Gamma_f}_{\Gamma_{f_1}\Gamma_{f_2}} g^G(\Gamma_{f_1}, \Gamma_{i_1}; \lambda) g^G(\Gamma_{f_2}, \Gamma_{i_2}; \lambda), \tag{A8}$$

where $n^{\Gamma_f}_{\Gamma_{f_1}\Gamma_{f_2}}$ are the numbers in the decomposition of the product $\Gamma_{f_1} \otimes \Gamma_{f_2}$ into irreducible representations [56] such that

$$\Gamma_{f_1} \otimes \Gamma_{f_2} = \sum_{\Gamma_f} n^{\Gamma_f}_{\Gamma_{f_1}\Gamma_{f_2}} \Gamma_f. \tag{A9}$$

In the particular case of invariants $\Gamma_f = A_1$ and formula (A8) simplifies into

$$g^G(A_1; \Gamma_{i_1} \oplus \Gamma_{i_2}; \lambda) = \sum_{\Gamma} g^G(\Gamma; \Gamma_{i_1}; \lambda) g^G(\Gamma^*; \Gamma_{i_2}; \lambda). \tag{A10}$$

If the initial representation is a direct sum of two representations we can distinguish Γ_{i_1} and Γ_{i_2} by different auxiliary variables. For example, instead of (A8) we can write

$$g^G(\Gamma_f; \Gamma_{i_1} \oplus \Gamma_{i_2}; \lambda, \mu) = \sum_{\Gamma_{f_1},\Gamma_{f_2}} C^{\Gamma_f}_{\Gamma_{f_1}\Gamma_{f_2}} g^G(\Gamma_{f_1}, \Gamma_{i_1}; \lambda) g^G(\Gamma_{f_2}, \Gamma_{i_2}; \mu). \tag{A11}$$

1. Concrete examples. Finite groups

Generating functions for the number of invariants and all possible covariants for all finite groups can be found in Ref. [48]. Below, we give several simple examples. The generating function for the totally symmetric representation (of any group) is trivial

$$g^G(A_1; A_1; \lambda) = \frac{1}{1-\lambda}. \tag{A12}$$

In particular this applies to group T_d if $\Gamma_{\text{initial}} = A_1$.

In the case of real one dimensional but not totally symmetric representation the generating function for invariants has the form

$$g^G(A_1; \Gamma; \lambda) = \frac{1}{1-\lambda^2}, \quad [\Gamma] = 1,\ \Gamma = \Gamma^*. \tag{A13}$$

whereas the generating function for the covariants of type Γ is

$$g^G(\Gamma; \Gamma; \lambda) = \frac{\lambda}{1-\lambda^2}, \quad [\Gamma] = 1,\ \Gamma = \Gamma^*. \tag{A14}$$

TABLE IV. Molien functions $g(\Gamma_{\text{final}};\Gamma_{\text{initial}};\lambda)$ for groups T_d and O.

$\Gamma_{\text{initial}} \backslash \Gamma_{\text{final}}$	A_1	A_2	E	F_1	F_2
F_1 [a]	$\frac{1+\lambda^9}{Z_1}$	$\frac{\lambda^3+\lambda^6}{Z_1}$	$\frac{\lambda^2+\lambda^4+\lambda^5+\lambda^7}{Z_1}$	$\frac{\lambda+\lambda^3+\lambda^4+\lambda^5+\lambda^6+\lambda^8}{Z_1}$	$\frac{\lambda^2+\lambda^3+\lambda^4+\lambda^5+\lambda^6+\lambda^7}{Z_1}$
F_2 [b]	$\frac{1}{Z_2}$	$\frac{\lambda^6}{Z_2}$	$\frac{\lambda^2+\lambda^4}{Z_2}$	$\frac{\lambda^3+\lambda^4+\lambda^5}{Z_2}$	$\frac{\lambda+\lambda^2+\lambda^3}{Z_2}$

[a] $Z_1 = (1-\lambda^2)(1-\lambda^4)(1-\lambda^6)$
[b] $Z_2 = (1-\lambda^2)(1-\lambda^3)(1-\lambda^4)$

TABLE V. Possible irreducible representations Γ_{final} for the pure normal-mode overtone states of AB_4 (T_d).

ν_k [a]	Γ_{i_k} [b]	$[\Gamma_{i_k}]$	Im [c]	λ_k [d]	Γ_{final}				
ν_1	A_1	1	C_1	(λ_1)	A_1				
ν_3	F_2	3	T_d	(λ_3)	A_1	A_2	E	F_1	F_2
ν_2	E	2	C_{3v}	(λ_2)	A_1	A_2	E		
ν_4	F_2	3	T_d	(λ_4)	A_1	A_2	E	F_1	F_2

[a] Spectroscopic notation of the mode.
[b] irreducible representation of T_d spanned by this mode.
[c] The image of T_d in the representation spanned by the mode.
[d] The auxiliary variable in the generating function.

In particular this is valid for group T_d or C_{3v} if $\Gamma_{\text{initial}} = A_2$.

Generating functions for the invariants and the two types of covariants of group C_{3v} constructed from the initial irreducible representation of type E have the form

$$g^{C_{3v}}(A_1;E;\lambda) = \frac{1}{(1-\lambda^2)(1-\lambda^3)}, \tag{A15a}$$

$$g^{C_{3v}}(A_2;E;\lambda) = \frac{\lambda^3}{(1-\lambda^2)(1-\lambda^3)}, \tag{A15b}$$

$$g^{C_{3v}}(E;E;\lambda) = \frac{\lambda+\lambda^2}{(1-\lambda^2)(1-\lambda^3)}. \tag{A15c}$$

The same formulae apply for group T_d in the case of $\Gamma_{\text{initial}} = E$. Finally, generating functions for $G = T_d$, and $\Gamma_{\text{initial}} = F_1$ and $\Gamma_{\text{initial}} = F_2$ are given in Table IV.

Let us now consider the situation where the initial representation Γ_{initial} is reducible and we should combine generating functions for each irreducible representation in Γ_{initial}, such as in Eqs. (A12), (A13), (A15), and Table IV. For this we use Eq. (A8) and the table of decomposition of the direct products of irreducible representations of the group G. As an example let us take a tetrahedral molecule AB_4. Excitations of each individual mode ν_k of symmetry Γ_{i_k} of this molecule can produce vibrational states, the so-called "overtones", with symmetries Γ_{f_k} listed in Table V.

If we, for example, construct a generating function for all bending vibrational states, i.e., for all states produced by excitations of ν_2 and ν_4, we consider $\Gamma_{\text{initial}} = \Gamma_{i_2} \oplus \Gamma_{i_4} = E \oplus F_2$. Numbers $n^{\Gamma_f}_{\Gamma_{f_2}\Gamma_{f_4}}$ for group T_d can be 0 or 1 [56]. All triples $(\Gamma_f, \Gamma_{f_2}\Gamma_{f_4})$ for which $n^{\Gamma_f}_{\Gamma_{f_2}\Gamma_{f_4}} = 1$ can be easily found from the decomposition of $\Gamma_{f_2} \times \Gamma_{f_4}$ for the group T_d:

Γ_f	A_1	A_2	E	F_1	F_2
$\Gamma_{f_2}\Gamma_{f_4}$	A_1A_1	A_1A_2	A_1E	A_1F_1	A_1F_2
	A_2A_2	A_2A_1	A_2E	A_2F_2	A_2F_1
	EE	EE	EA_1	EF_1	EF_2
			EA_2	EF_2	EF_1
			EE		

TABLE VI. Character table for the $D_{\infty h}$ group.

$D_{\infty h}$	E	$2C(\phi)$	$\infty\sigma_v$	i	$2[iC(\phi)]$	∞C_2
$\Sigma_g^+ = A_{1g}$	1	1	1	1	1	1
$\Sigma_g^- = A_{2g}$	1	1	-1	1	1	-1
E_k^g [a]	2	$2\cos(k\phi)$	0	2	$2\cos(k\phi)$	0
$\Sigma_u^+ = A_{1u}$	1	1	1	-1	-1	-1
$\Sigma_u^- = A_{2u}$	1	1	-1	-1	-1	1
E_k^u	2	$2\cos(k\phi)$	0	-2	$-2\cos(k\phi)$	0

[a] $k = 1, 2, ...$ is a positive integer. Alternative notation: $E_1^\alpha = \Pi_\alpha$, $E_2^\alpha = \Delta_\alpha$, etc

TABLE VII. Generating functions for the $D_{\infty h}$ group.

	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	E_{2k}^g	E_{2k+1}^g	E_{2k}^u	E_{2k+1}^u
$g(\Gamma; \Pi_u; \lambda)$	$\frac{1}{1-\lambda^2}$	0	0	0	$\frac{\lambda^{2k}}{1-\lambda^2}$	0	0	$\frac{\lambda^{2k+1}}{1-\lambda^2}$
$g(\Gamma; \Sigma_g^+; \lambda)$	$\frac{1}{1-\lambda}$	0	0	0	0	0	0	0
$g(\Gamma; \Sigma_u^+; \lambda)$	$\frac{1}{1-\lambda^2}$	$\frac{\lambda}{1-\lambda^2}$	0	0	0	0	0	0

2. Concrete examples. Continuous groups.

The calculation of Molien functions in the case of continuous symmetry groups is slightly different from the case of finite groups. The expression for the Molien function (A1) should be modified. We replace the sum over group elements by the integral over the group and the order of the finite group by the volume

$$g(\Gamma_f; \Gamma_i; \lambda) = \frac{1}{V_G} \int_G d\tau \frac{\chi_g^{(\Gamma_f)*}}{\det(E - \lambda X_g^{(\Gamma_i)})}. \tag{A16}$$

Below we give the example of this calculation for a linear molecule AB_2 with symmetry group $D_{\infty h}$.

Vibrational modes of the AB_2 ($D_{\infty h}$) molecule span the four dimensional representation $\Gamma_0 = \Sigma_g^+ + \Sigma_u^+ + \Pi_u$. The generating function for the number of tensors constructed from this reducible representation can be easily found by using (A11) and generating functions for irreducible representations. The only nontrivial step is to calculate the generating function for tensors constructed from the Π_u representation. Taking into account the table of characters for the $D_{\infty h}$ group, given in Table VI to avoid possible discrepancy in notation of elements and representations, we get the following generating function

$$g(\Gamma_f; \Pi_u; \lambda) = \frac{1}{8\pi} \left(\int_0^{2\pi} \frac{d\phi \chi^{(\Gamma_f)}(C(\phi))}{1 - 2\cos\phi\lambda + \lambda^2} + \int_0^{2\pi} \frac{d\phi \chi^{(\Gamma_f)}(\sigma_v)}{1-\lambda^2} + \int_0^{2\pi} \frac{d\phi \chi^{(\Gamma_f)}(iC(\phi))}{1 + 2\cos\phi\lambda + \lambda^2} + \int_0^{2\pi} \frac{d\phi \chi^{(\Gamma_f)}(C_2)}{1-\lambda^2} \right). \tag{A17}$$

All generating functions for group $D_{\infty h}$ with all Γ_f and $\Gamma_i = \Sigma_g^+, \Sigma_u^+, \Pi_u$ are given in Table VII. The combination of generating functions enables us to write the three parameter generating functions for the initial representation Γ_0 [Eqs. (30) and (31)] which are used in the main body of the paper to calculate differential densities of vibrational states for the linear molecule CS_2.

APPENDIX B: EXPLICIT FUNCTIONAL FORM OF THE COEFFICIENTS OF THE TAYLOR EXPANSION OF GENERATING FUNCTIONS

Consider a generating function of the form

$$g(\lambda) = \frac{P(\lambda)}{(1-\lambda^{n_1})\dots(1-\lambda^{n_k})}, \tag{B1a}$$

where $P(\lambda)$ is a polynomial, and all n_i are positive integers. We construct such function $C(N)$ that for all integer $N \geq 0$ its value equals the coefficients C_N in the formal expansion

$$g(\lambda) = \sum_N C_N \lambda^N = \sum_N C(N) \lambda^N. \tag{B1b}$$

In the particular case, if all $n_i = t$ and $P(\lambda) = \lambda^s$ with $s < t$, we find the following correspondence between the generating function and its $C(N)$ function

$$\frac{\lambda^s}{(1-\lambda^t)^v} \quad \Longrightarrow \quad \frac{((N-s)/t + v - 1)!}{((N-s)/t)!(v-1)!} \, \delta_{s, N \bmod t}. \tag{B2}$$

Here $\delta_{s,u}$ equals 1 if $s = u$ and 0 otherwise, and the notation $N \bmod t$ means that N is taken modulo t. For $t = 1$ ($N \bmod 1 = s = 0$), the $C(N)$ function in (B2) is a polynomial of degree $k-1$ whose coefficients are rational numbers. We call such polynomials "regular". For $t > 1$ this function is a polynomial of degree $k-1$ whose coefficients are t-periodic in N. We call such polynomials "oscillatory".

The key point is that the general function (B1a) can always be represented as a sum

$$\frac{P(\lambda)}{(1-\lambda^{n_1})\ldots(1-\lambda^{n_k})} = \sum_t \sum_{v=1}^{V(t)} \frac{P_{t,v}(\lambda)}{(1-\lambda^t)^v}, \tag{B3}$$

and therefore its $C(N)$ function is a combination of elementary functions in the rhs of (B2). The degree of polynomials $P_{t,v}(\lambda)$ is at most $t-1$. The index t runs over the set of all numbers that are divisors of at least one of $n_1, n_2, \ldots, n_k$, including $t = 1$ and any of n_i's. Index v takes all integer values from 1 to $V(t)$. The upper bound $V(t)$ equals the number of different n_i that divide by t. It is clear that for the $1/(1-\lambda)^v$ terms $1 \le v \le V(1) = k$ [k is the number of factors $(1-\lambda^{n_i})$ in the denominator of the initial generating function]. Despite all imposed restrictions on v and t the transformation (B3) and, therefore, the form of the $C(N)$ function is still not unique. Nevertheless any representation (B3) gives the same values C_N. To eliminate the ambiguity we should further restrict the degree of polynomials $P_{t,v}$. Thus, for all $t > 1$ the degree of $P_{t,v}$ can always be taken as $t-2$; it can be taken even smaller if t is not prime.

As an example we transform the generating function $g_{2:2:2:2:1:1:1:1:1}(\lambda)$ defined in Eq. (12) in the main body of the paper.

$$\begin{aligned}\frac{1}{(1-\lambda^2)^4(1-\lambda)^5} &= \frac{1}{16(1-\lambda)^9} + \frac{1}{8(1-\lambda)^8} + \frac{5}{32(1-\lambda)^5} + \frac{5}{32(1-\lambda)^6} + \frac{35}{256(1-\lambda)^5} + \frac{55}{512(1-\lambda)^4} \\ &+ \frac{75}{1024(1-\lambda)^3} + \frac{75}{2048(1-\lambda)^2} + \frac{1}{32(1-\lambda^2)^4} + \frac{5}{128(1-\lambda^2)^3} + \frac{5}{128(1-\lambda^2)^2} + \frac{75}{2048(1-\lambda^2)}.\end{aligned} \tag{B4}$$

Substitution of (B2) into (B4) gives the $C(N)$ function in Eqs. (24) and (25).

To give a more complicated example we take the generation function

$$g_{10:6:6:23}(\lambda) = \frac{1}{(1-\lambda^{10})(1-\lambda^6)^2(1-\lambda^{23})} \tag{B5}$$

in Table II, inspired by the CS_2 molecule [51]. The decomposition of (B5) into elementary fractions (B3) gives polynomials $P_{t,v}(\lambda)$ listed below.

$t \backslash v$	1	2	3	4
23	$(\lambda^{21} + 29\lambda^{20} + 35\lambda^{19} + \ldots)/23$			
10	$(-\lambda^4 - 2\lambda^3 + 2\lambda^2 + \lambda - 2)/5$			
5	$(\lambda^3 - \lambda^2 + 1)/5$			
6	$(-95\lambda^2 - 13\lambda + 79)/54$	$-\lambda(\lambda+1)/3$		
3	$(-11/18\lambda - 28/27)$	0		
2	821/2160	13/120	1/90	
1	0	619/49680	1/920	1/8280

The set of all divisors of the exponents in (B5) is $[(1,2,5,10);(1,2,3,6);(1,2,3,6);(1,23)]$. Consequently, $t = 1,2,3,6,5,10,23$, and $V(1) = 4$, $V(2) = 3$, and $V(3) = V(6) = 2$. As a result, the regular part of $C(N)$ is a polynomial in N of degree 3, the quadratic-in-N terms have oscillating part with period 2, and the linear-in-N terms have oscillating part with period 6. Finally the constant term has the period $23 \cdot 5 \cdot 3 \cdot 2 = 690$ (the least common multiple of all exponents). All these different contributions to the $C_{10:6:6:23}(N)$ are shown in Fig. 7 (cf. Table II).

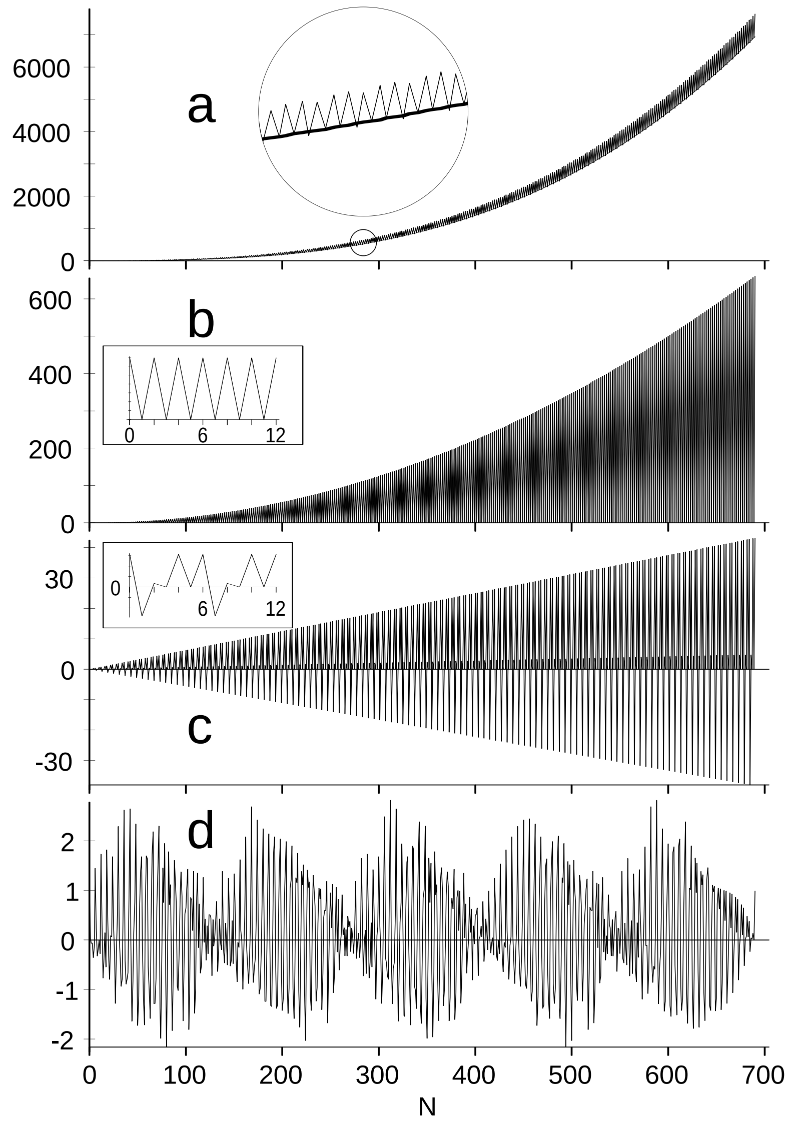

FIG. 7. Function $C_{10:6:6:23}(N)$ for generating function $g_{10:6:6:23}(\lambda)$ in (B5): (a) total function with the regular part shown in the zoomed part, (b) quadratic-in-N oscillatory part, (c) linear-in-N oscillatory part, (d) N-independent period-690 oscillation. The fragments in (b) and (c) show the actual form of oscillation of the coefficient before, respectively, N^2 and N^1.

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[7] By ν_i and N_i we denote the frequency of the vibrational mode i and the number of quanta in this mode. Then ν, ν_0, and the energy $E(N)$, such as in Eqs. (15) and (44), are also in units of frequency, or we can equally assume $h = 1$.
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$$\frac{1}{(1-\lambda)^K} = \sum_{N=0}^{\infty} \binom{K-1+N}{K-1} \lambda^N,$$

are exactly (3b).
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