

# Direct absorption transitions to highly excited polyads 8, 10, and 12 of methane

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We report on the first experimental observation of high-resolution rotationally resolved spectra of vibrational polyads 10 and 12 of methane lying approximately half way to the dissociation energy. The spectra were obtained at 295 K and 124 K and pressures as low as 200 mbar using a highly sensitive laser-induced gratings (LIGs) technique. They correspond to direct single-photon absorption transitions from the ground state with cross-sections as low as  $10^{-25}$  to  $10^{-26}$  cm<sup>2</sup> molecule<sup>-1</sup>. We discuss theoretical developments towards the complete analysis of these transitions.

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## I. INTRODUCTION

Spectra of very weak absorption transitions have been for a long time our principal source of information on specific molecular states or on conditions (pressure, temperature) in situations when usual dipole transitions are inaccessible (due to saturation, for example) or forbidden. Such are the well known cases in planetary science, astrophysics, atmospheric observations, and plasma studies.

The weak absorption transitions that we study here are of a rather general nature. Their probabilities are extremely weak not due to a specific property of the particular quantum molecular system (symmetry, spin, etc) but because the absorbed photon increases the vibrational quantum number  $v$  associated with the affected vibrational degree(s) of freedom by a number of quanta  $n \gg 1$ , while in the usual allowed absorption transition  $v$  increases just by 1. For weak classical fields, the very small probability of such an event is described by the  $n$ -th Taylor series term of the effective dipole moment (see Sec. IV). These types of transitions with the maximal value  $n_{\text{act}}$  of the number of quanta of the dipole-active mode running as high as 6–7 were observed in a number of molecules, notably CO, CO<sub>2</sub>, ozone, and methane (polyads  $P_n$  with  $n = 2n_{\text{act}}$ )—all of great importance to various fields mentioned above as well as to the molecular theory itself.

With recent advancements of spectroscopic techniques, it has become possible to reproduce these transitions *in vitro* at maximal spectral resolution. Thus in Ref. [1], we demonstrated the spectroscopic potential of the laser-induced gratings (LIGs) technique on the example of the  $P_0 \rightarrow P_8$  near-IR transition of methane. Most recently, we observed similar transitions to polyads  $P_{10}$  and  $P_{12}$  [2], see Fig. 1. The purpose of our paper is to show how our and similar new experiments bring a standard spectroscopic study into the mainstream of the contemporary physics, and to assess the theoretical work required for the satisfactory understanding of these data.

We realize that for a number of reasons, the required

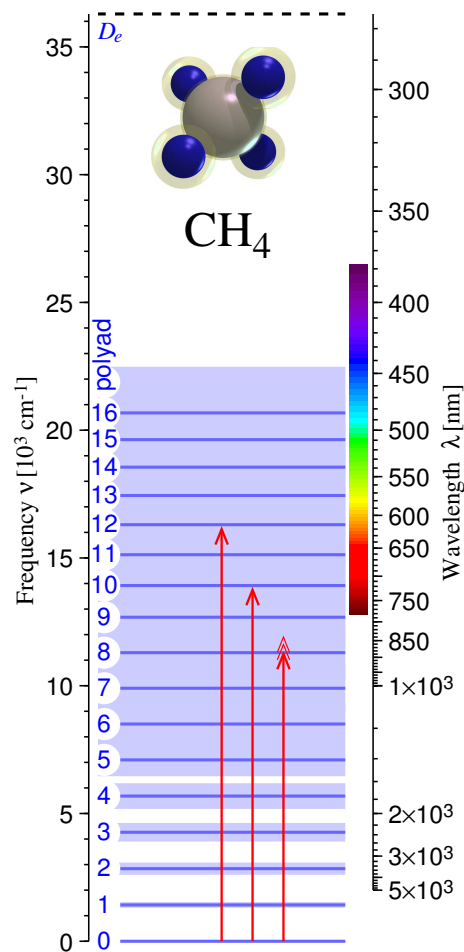


FIG. 1: Polyads of methane and transitions discussed in this work

theory should go significantly beyond standard techniques of molecular spectroscopy, and that a detailed traditional line-by-line analysis and a spectroscopic fit to a Taylor series phenomenological model may be but a very distant possibility. The main issue is in preparing the foundation for such a future analysis. Typically,

spectroscopists base their description on small groups of vibrational states which they can describe by reasonably compact phenomenological models. The classification of the states begins with the ground state, i.e., the framework of small vibrations about the equilibrium is assumed. We cannot continue this scheme to the states involved in our experiments. Figuratively speaking, we should find instead a different starting point for the series approximation. We believe that this point can be found by replacing “static” equilibrium-based linear vibrational normal mode theory for dynamical nonlinear analysis that can select stable highly nonlinear localized vibrations. Though the idea itself is not entirely new, we like to draw more attention to this problem and to set up the framework of thinking that may lead to a satisfactory physical explanation and the eventual quantitative analysis.

### A. Vibrational levels of methane

Methane ( $\text{CH}_4$ ) is a light highly symmetric five-atomic molecule. The spatial symmetry group of its rovibrational Hamiltonian is the tetrahedral group [61]  $T_d$  of order 24; the full symmetry group  $T_d \times \mathcal{T}$  [3] which includes time-reversal  $\mathcal{T}$  is isomorphic to  $O_h$ . This group has two important classes of subgroups which we refer to as  $D_{2d}$  and  $C_{3v}$  and which are built around four-fold and three-fold axes, respectively, see Fig. 2. Methane has nine vibrational degrees of freedom combining into four vibrational normal modes:  $\nu_1$  (of symmetry type  $A_1$ , or the fully symmetric mode),  $\nu_2$  ( $E$ ),  $\nu_3$  ( $F_2$ ), and  $\nu_4$  ( $F_2$ );  $\nu_1$  and  $\nu_3$  are stretching modes,  $\nu_2$  and  $\nu_4$  are bending modes. The ratio of the harmonic frequencies of these modes

$$\omega_1 : \omega_2 : \omega_3 : \omega_4 \approx 2 : (1:1) : (2:2:2) : (1:1:1) \quad (1)$$

is typical for small molecules and can be considered as a multidimensional Fermi resonance. Due to this resonance, quantum vibrational states with the same

$$n = 2n_1 + n_2 + 2n_3 + n_4, \quad (2)$$

where  $n_k$  is the number of quanta in mode  $k$ , form quasidegenerated *polyads*  $P_n$  labeled by polyad quantum number  $n$ . Vibrational polyads exist in many molecules ( $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{O}$ , etc). The specifics here is in the presence of several degenerate vibrations which may be considered as exact resonances. Such highly degenerate situation exacerbates the problem of classifying and selecting desired states within a polyad. The analysis is certainly made quite complicated due to the large total number  $K = 9$  of vibrational degrees of freedom involved. This kind of studies is more common for  $K = 2$  or  $3$  where we can rely more on physical intuition. Furthermore, the high symmetry of the system imposes the use of certain mathematical methods which are less important in other systems. These technical details can be found elsewhere [3, 4] and we keep them to a minimum.

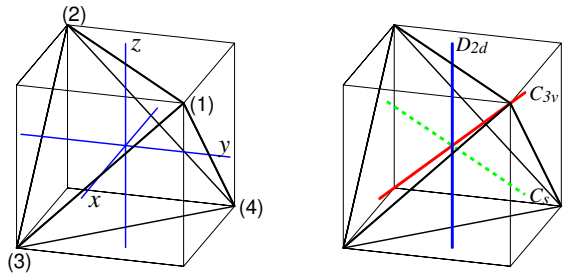


FIG. 2: Coordinates in  $\mathbb{R}^3$  and symmetry axes of a tetrahedron

The ground state of methane  $P_0$  and the first two polyads [62], the *dyad*  $P_1$  and *pentad*  $P_2$ , have been studied extremely well [4–6].  $P_1$  is formed by bending fundamentals  $\nu_2$  and  $\nu_4$ , while pentad includes stretching fundamentals  $\nu_1$  and  $\nu_3$ , and bending overtones  $2\nu_2$ ,  $\nu_2 + \nu_4$ , and  $2\nu_4$ . The analysis of the *octade*  $P_3$ , can still be regarded as sufficiently complete [7, 8], and very satisfactory progress has been made in the study of  $P_4$  which includes first overtones of stretching modes  $2\nu_1$ ,  $\nu_1 + \nu_3$ , and  $2\nu_3$ . Higher polyads remain a widely open field. The number of rotational levels there is so large that their complete assignment can hardly be imagined at present. At the same time, the potential well of methane is very deep, and even polyad  $P_{10}$  situated at about  $14\,000\text{ cm}^{-1}$  is not even half way to the first dissociation energy  $D_e$  of approximately  $35\,000\text{ cm}^{-1}$  (for  $\text{CH}_3\text{-H}$ ) [9], see Fig. 1.

In the last decade, extensive computations [10–15] have been attempted in order to climb up this vibrational potential in various ways. However, the analysis of the actual dynamics of this excited system with strongly interacting nine degrees of freedom did not follow. It is likely that the concepts of relative equilibrium and nonlinear normal mode [63] generalizing the more intuitive and simple molecular ideas of local mode and chromophore, are still not fully appraised in molecular physics. Yet it is on these more general and truly dynamical concepts that our progress depends entirely in the case of methane.

### B. Spectra and their tentative assignment

We survey briefly what has been done before us. Since the mid-90’s, a variety of methods has been developed and applied for extended high resolution and low rotational temperature investigations of weak overtone and combination absorption transitions to the high lying vibrational states of methane. In particular, three features of the methane spectrum have been observed in the near-IR spectral range of 889, 861 and 840 nm (between  $11\,170$  and  $11\,980\text{ cm}^{-1}$ ). These bands are the most prominent features of the  $P_0 \rightarrow P_8$  transition. Intracavity photoacoustic and tone-burst modulation spectroscopy [16–18], and intracavity laser absorption [19], were used to study

methane bands around  $11300\text{ cm}^{-1}$ . In addition, the high sensitivity of the intracavity laser absorption technique has been employed to measure absorption spectra and coefficients between  $10635$  and  $13300\text{ cm}^{-1}$  [20]. Later, the spectral region around  $11900\text{ cm}^{-1}$  has been investigated by applying wavelength modulated diode laser spectroscopy [21]. Recently in Ref. [1], we have applied laser-induced gratings (LIGs) spectroscopy, a non-linear technique using resonances of linear absorption, for the investigation of these absorption bands with resolution of about  $0.04\text{ cm}^{-1}$ .

The most prominent band of the  $0 \rightarrow P_8$  spectrum at  $889\text{ nm}$  is similar to the  $P_{10}$  and  $P_{12}$  transitions that we describe here in Sec. II. The presence of this relatively simple and compact strong band is striking. This band is tempting to be assigned as a transition to a single vibrational “bright” upper state, which Giver [22] and later Boraas et al. [16] assigned tentatively as the  $3\nu_1 + \nu_3$  stretching combination overtone strongly coupled to several “dark” close-lying states. The weaker  $861$  and  $840\text{ nm}$  features were attributed to the combination bands  $2\nu_1 + 2\nu_3$  and  $\nu_1 + 3\nu_3$ , respectively. This assignment persisted in later work [17–21].

Admittedly, the  $3\nu_1 + \nu_3$  normal mode assignment simplified the spectroscopic analysis because the rotational structure of the  $0 \rightarrow 3\nu_1 + \nu_3$  transition resembles that of the  $0 \rightarrow \nu_3$  fundamental. However, the presence in  $P_8$  of such a predominantly stretching normal mode overtone seems unlikely because of strong couplings between the modes. Thus already in  $P_4$ , the stretching overtones  $2\nu_1$ ,  $\nu_1 + \nu_3$ , and  $2\nu_3$  have the respective normal mode content at the level of only 70% (see Table 4 in Ref. [7]) and this percentage drops quickly in higher polyads [64]. So more generally, we may interpret the bright  $P_8$  state as a *localized vibrational state* (of predominantly stretching nature if we want to accommodate for Ref. [16–18]).

Unlike its cousins with heavier central atom (Si, Ge) [23–27], methane is not known to have true *local mode* states [10, 12, 13]. It may, nevertheless, have vibrational localization of a more complex, dynamical nature. So *our immediate goal* is to understand whether vibrational localized states of any kind, and purely stretching ones in particular, can show up in highly excited polyads of methane (see more in Sec. II C).

## II. OBSERVED SPECTRA

In this work, we present higher frequency absorption spectra of methane recorded using the LIGs technique in the  $727\text{ nm}$  (Fig. 3) and  $619\text{ nm}$  (Fig. 4) regions, corresponding to the transitions  $P_0 \rightarrow P_{10}$  and  $P_0 \rightarrow P_{12}$ , respectively [2]. Following the tradition, one may like to assign these spectra to combination bands  $4\nu_1 + \nu_3$  and  $5\nu_1 + \nu_3$ .

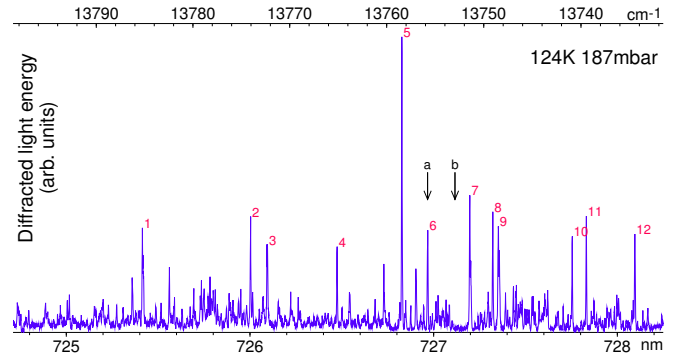


FIG. 3: The central part of the LIG absorption spectrum [2] of the  $P_0 \rightarrow P_{10}$  transition in methane recorded at  $124\text{ K}$  and  $187\text{ mbar}$  with spectral resolution of  $0.04\text{ cm}^{-1}$ ; the “zero signal” line coincides with the nm axis. The arrows (a) and (b) point to the pump wavelengths  $\lambda_p$  for the resonant and nonresonant signal temporal profiles in Fig. 5.

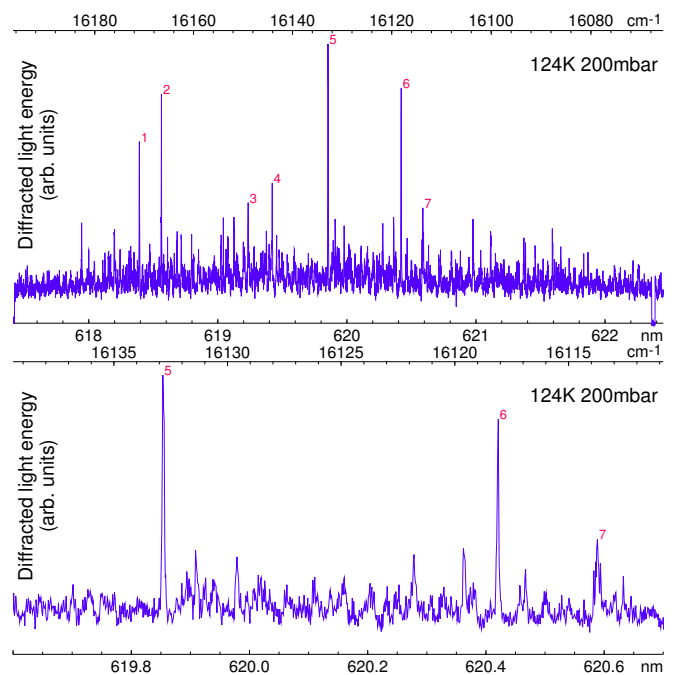


FIG. 4: The central part (top) and its blowup (bottom) of the LIG absorption spectrum [2] of the  $P_0 \rightarrow P_{12}$  transition in methane recorded at  $124\text{ K}$  and  $200\text{ mbar}$  with spectral resolution of  $0.04\text{ cm}^{-1}$ ; the “zero signal” line coincides with the nm axis.

### A. Laser-induced gratings

In general, laser-induced gratings are spatially-periodic variations of the complex refractive index of the medium. General information on LIGs in various media can be found in Ref. [1] and references therein. If molecules are resonantly excited by a short-pulse radiation in the interference region of two pump laser beams at wavelength  $\lambda_p$ , which are crossed at the angle  $2\theta_p$ , a spatially-periodic variation of the population of the energy levels involved

TABLE I: Principal features of direct absorption transitions to polyads 10 and 12 of methane at low temperature [2]. Line numbers (#) correspond to those indicated in Fig. 3 and 4; respectively, line intensities  $I$  are given in relative units.

$P_0 \rightarrow P_{10}$		$P_0 \rightarrow P_{12}$			
#	$\lambda$ [nm]	$I$	#	$\lambda$ [nm]	$I$
1	725.414	35	1	618.392	67
2	726.003	39	2	618.563	83
3	726.095	29	3	619.234	46
4	726.474	29	4	619.421	52
5	726.826	100	5	619.853	100
6	726.967	34	6	620.420	85
7	727.196	46	7	620.588	44
8	727.322	40			
9	727.352	36			
10	727.754	32			
11	727.831	39			
12	728.095	33			

is produced. The period of the spatial modulation equals to the interference fringe spacing,  $\Lambda = \lambda_p / (2 \sin \theta_p)$ . Fast collisional deactivation of the excited states may provide a corresponding modulation of the refractive index resulting from local temperature and density variations and thus lead to the formation of so-called *thermal* LIGs. Adiabatic compression of the gas by the spatially inhomogeneous pump electromagnetic field strength, simultaneous with resonant excitation, generates nonresonant *electrostrictive* LIGs. LIGs are usually registered by detecting the part of read-out laser radiation which crosses the pump beams interaction region and is diffracted by the modulations of the complex refractive index. For efficient diffraction, the read-out, or probe beam, at wavelength  $\lambda_r$ , should be directed to the planes of the fringes at the Bragg angle  $\theta_r$ , defined as  $\sin \theta_r = \lambda_r / (2\Lambda)$ . If a continuous-wave (cw) probe radiation is employed, the temporal evolution of diffraction efficiency of a short-pulse excited LIG can be recorded. A pulse of the diffracted light registered by a photodetector generates the characteristic LIG signal  $S(t)$ .

A typical resonant signal observed in the  $P_0 \rightarrow P_{10}$  band of  $\text{CH}_4$  (at 187 mbar and 124 K) is presented in Fig. 5a. It was recorded after tuning the pump wavelength  $\lambda_p$  to the resonance with the transition at 726.967 nm (line 6 in Fig. 3 and Table I). The signal oscillations in this figure correspond to the variations of the refractive index caused by spatially-periodic acoustic waves and stationary density modulations. Both are induced by rapid collisional deactivation of the excited  $\text{CH}_4$  molecules, and the signal's temporal profile is characteristic for that determined by the thermal LIGs. The period of the oscillations of about 120 ns and the signal decay scale of a few microseconds are determined by the fringe spacing  $\Lambda$  and the sound velocity. Spectroscopy of the absorption transitions is accomplished by means of tuning the pump laser frequency through the range

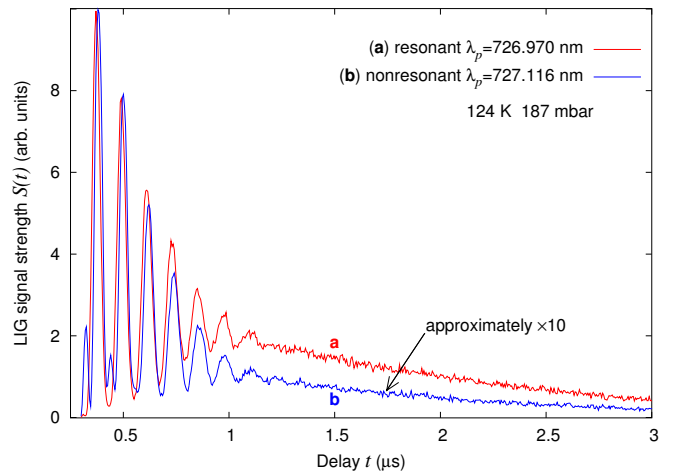


FIG. 5: Typical temporal profiles of the LIG signals recorded in the  $P_0 \rightarrow P_{10}$  band of  $\text{CH}_4$  (187 mbar, 124 K, cf Fig. 3) for (a) resonant excitation at pump wavelength  $\lambda_p = 726.967$  nm (line 6 in Fig. 3 and Table I), and (b) nonresonant excitation at  $\lambda_p = 727.116$  nm, in the region of weak absorption.

of interest and measuring the peak value of  $S(t)$ , or its integral within a definite time interval, as a function of frequency.

## B. Experimental details

The experimental set-up employed in this work has been described previously [1]. In brief, the output radiation of a 20 Hz repetition rate narrow-band tunable dye laser providing up to 25 mJ/pulse was employed as a pump source. Pulse duration was approximately 10 ns and a spectral bandwidth was  $\approx 0.04 \text{ cm}^{-1}$ . (To obtain coherent radiation in the near-infrared region of 835–895 nm, the frequency of the dye laser was Raman shifted in a 1.5 m length cell containing  $\text{H}_2$  at 5 bar). The dye laser was pumped by the frequency-doubled radiation of a Nd:YAG laser. The pump radiation was split into a pair of roughly equally intense LIG excitation beams with parallel polarizations. These beams were subsequently focused by a lens ( $f = 900$  mm) and intersected at the crossing angle of  $2\theta_p \approx 1.20^\circ$  (see Fig.6) that provides a fringe spacing of  $\Lambda \approx 35 \mu\text{m}$  at  $\lambda_p = 727$  nm. A wavemeter with the specified accuracy of  $10^6$  is used to measure the absolute excitation wavelength in each pulse.

The LIGs are read out by utilizing the beam of an  $\text{Ar}^+$ -laser delivering up to 1.1 W at 514.5 nm. The cw probe beam is propagating parallel to the pump beams and focused by the same lens into the interaction region at a Bragg angle of  $\theta_r = 0.42^\circ$ . In this manner, a 3D forward phase-matching geometry is arranged (see Fig.6). The diffracted light is spatially filtered and coupled into a multimode fused silica fiber delivering it to a fast photomultiplier. Additional stray-light reduction is achieved by using a band-pass interference filter cen-



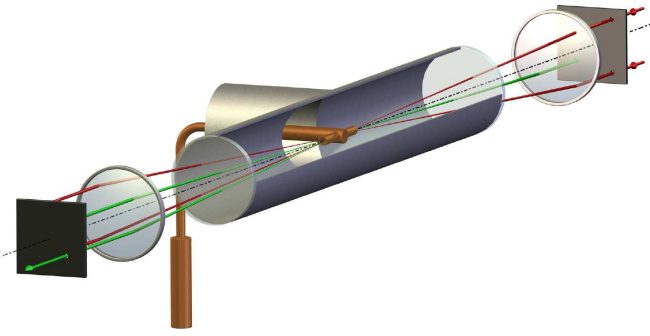


FIG. 6: The focusing geometry of the pump, probe and signal beams in the LIGs experiment; the gas cell with the cold finger are represented schematically.

tered at the read-out laser wavelength and placed in front of the photomultiplier. Temporally resolved acquisition of the LIG signals, single-shot or averaged, is performed by using a digital oscilloscope with an analog bandwidth of 1 GHz and a sampling rate up to 4 GS/s. The signals are recorded during 2–10  $\mu\text{s}$ , depending on pressure. Spectra are obtained by scanning the frequency of the dye laser radiation and accumulating the LIG signal integrated within an optimized time interval after the excitation pulse. The spectral resolution of about  $0.04\text{ cm}^{-1}$  has been provided.

The gas cell used in our experiments could be evacuated to less than  $10^{-4}$  bar and allowed to work with gas pressures up to 5 bar. Gas pressure in the sample volume was measured by a capacitance manometer. A copper cold finger cooled by liquid nitrogen was mounted to enter into the cell (see Fig.6). The sample volume, with the dimensions of about 0.3 mm in diameter and 20 mm in length, was located at the axis of a narrow (5 mm in diameter and 30 mm in length) channel through the cold finger. The channel wall temperature was measured by a thermocouple. The measurements in the gas cell were performed at  $\text{CH}_4$  pressures of 0.2–4 bar and temperatures 298 K and 124–130 K. Methane of quality 2.5 (Messer-Griesheim) has been used for the measurements.

### C. Spectra and their assignment. The main objective of the work

In the rotational structure of spectra  $P_0 \rightarrow P_n$  with  $n = 8, 10, 12$ , we distinguish immediately two kinds of lines: a relatively small number of prominent lines (Table I) forming a 100–200  $\text{cm}^{-1}$  (several nm's at these frequencies) large band, and a very dense broader “undergrowth” of much weaker numerous overlapping lines (see Fig. 3 and 4). All these lines rise above a structureless background which can be particularly well observed in Fig. 4 where the actual zero-absorption signal level is coincident with the nm axis. To study the background, we tuned the pump frequency away from single sharp lines and recorded the temporal profiles of the LIG signal.

From these experiments (see Fig. 5b), we can conclude that the background signal, though being about an order of magnitude weaker and hence demonstrating noticeable nonresonant contribution from the electrostrictive LIG (seen as smaller oscillation peaks), is nevertheless caused primarily by the thermal LIGs which result from the *resonant* absorption of the pump radiation.

The conclusion, plausible to anyone well familiar with the rotation-vibration bands of methane, is that the prominent lines represent rotational levels of one single or, at most, a few “bright” vibrational states, while the weaker lines *and* the background result from a very dense spectrum of surrounding “dark” states coupled to the bright ones through various vibrational and rovibrational mechanisms.

In order to simplify the spectra and to facilitate the eventual identification of the spectral lines, we attempted to reduce the number of the populated rotational ground state levels by the cryogenic cooling of the small sample volume in the middle of the gas cell (see Fig. 6) to temperatures  $T \approx 120$  K. Note that the angular momentum  $J_{\text{max}}$  of the most populated rotational ground state level of  $\text{CH}_4$  can be estimated as  $J_{\text{max}} \approx \sqrt{kT/hcB}$ , where  $B \approx 5.24\text{ cm}^{-1}$  is the rotational constant of the molecule. So lowering  $T$  from 295 K to 124 K brought  $J_{\text{max}}$  down from 6 to 4. We have also observed, that the number of the strongest visible lines in the cold gas spectra appears to decrease with growing polyad number  $n$  (pump radiation frequency).

The dense spectrum of the second kind is expected. Indeed, at these excitation energies, just the density of vibrational states is approximately one or several states per  $\text{cm}^{-1}$ , the splittings are less than characteristic interaction terms, and all these states are typically mixing well with each other. We are in the semiclassical domain and the dynamics of the classical limit system at these energies is significantly irregular.

On the other hand, the existence of such a relatively small number of very bright states is fascinating. How is it possible for the specific absorption process to be so selective? There are two aspects to this question: the nature of the excited state and the absorption process itself. We address them in Sec. III and IV, respectively. Both aspects surpass considerably the domain of a traditional spectroscopic study. Answering the first part involves analyzing possibilities of regular motions in a strongly perturbed nonlinear dynamical system with many degrees of freedom and the corresponding localization in the quantum analogue system. The second part requires detailed understanding of the specific interaction of such a system with light under essentially semiclassical conditions.

## III. VIBRATIONAL POLYADS OF METHANE

We turn to the first part of the question: what subset of the vibrational states of the polyad  $P_n$  is involved in the observed transitions  $P_0 \rightarrow P_n$  with large  $n = 8, 10, 12$ ?

Is it a small group of well localized excited states? If yes, what is its nature? If no, why is the rotational structure of the spectrum so “simple”? After recalling pertinent details of the polyad theory in Sec. III A, we address these questions in Sec. III C. The theory in Secs. III A and III B is presented sketchily at the medium-to-advanced level. Some of the details are relatively standard and may serve as a checklist or can be skipped altogether at first reading. Specific material begins with Sec. III A 6 and continues across Sec. III B.

### A. General outline for the polyad approximation

Consider the original classical dynamical system which represents vibrations of the molecule with  $K$  vibrational degrees of freedom [65]. In the most standard setup, coordinates  $Q$  in  $\mathbb{R}^K$  describe small distortions of the equilibrium geometric configuration of the molecule (in the given electronic state) at  $Q = 0$ . The dynamics takes place on the phase space  $T\mathbb{R}^K$  with dynamical variables  $(P, Q)$  and standard symplectic structure  $dP \wedge dQ$ . The energy is given by the vibrational Hamiltonian  $H(Q, P)$  with an elliptic equilibrium at  $Q = P = 0$ .

#### 1. Resonances and polyads

The origin of polyads is in the (near) *resonance*

$$k_1^{-1} \omega_1 \approx k_2^{-1} \omega_2 \approx \dots \approx k_K^{-1} \omega_K \approx \omega_0$$

of the frequencies  $\omega_i$  with  $i = 1, \dots, K$ , of the linearization of this system at  $P = Q = 0$ , i.e., of the harmonic frequencies of the quadratic Hamiltonian

$$H_0(Q, P) \approx \omega_0 \mathcal{N}(Q, P),$$

where

$$H_0(Q, P) = \frac{1}{2} \sum_i^K \omega_i (P_i^2 + Q_i^2), \quad \text{and}$$

$$\mathcal{N}(Q, P) = \frac{1}{2} \sum_i^K k_i (P_i^2 + Q_i^2) = \sum_i^K k_i N_i.$$

The polyad approximation is enforced by normalizing  $H(Q, P)$  with respect to the flow  $\varphi_{\mathcal{N}}^t$  of the Hamiltonian vector field  $X_{\mathcal{N}}$  of the polyad integral  $\mathcal{N}(Q, P)$ . This involves a near-unity canonical transformation  $(Q, P) \mapsto (q, p)$  and gives the *normal form*  $\mathcal{H}(q, p)$  which depends on the dynamical variables  $(q, p)$  of the normalized system.

#### 2. Reduction of polyad symmetry

The normalized system still has  $K$  degrees of freedom, but it now has a built-in strict  $\mathbb{S}^1$  Lie symmetry which is

given by  $\varphi_{\mathcal{N}}^t$  and which acts on the phase space  $T\mathbb{R}^K$  so that  $\mathcal{H}(q, p)$  remains invariant. Note that because it is defined by a Hamiltonian flow (as opposed, for example, to an  $\text{SO}(2)$  rotation symmetry group acting on the configuration space), this symmetry is called *dynamical*; since it defines quantum polyads, it is called *polyadic*; since the resonance condition is not exact and higher orders in the initial  $H(Q, P)$  are not invariant with respect to this symmetry, it is *approximate*. Reducing the polyadic symmetry, we eliminate the associated universal polyad degree of freedom. Technically, in the process of reduction, the polyad integral  $\mathcal{N}(q, p)$  is replaced by its value  $n \geq 0$  which becomes a *parameter*. In that way, we obtain *reduced* Hamiltonian  $\mathcal{H}_n$  on the compact reduced phase space  $\mathcal{P}_n$  of real dimension  $2K - 2$  called *polyad space*. Each point of  $\mathcal{P}_n$  lifts to a circular orbit  $\gamma_n \subset T\mathbb{R}^K$  of  $\varphi_{\mathcal{N}}^t$ , or an  $\mathcal{N}$ -orbit for brevity.  $\mathcal{P}_n$  is generally a weighted projective space on which the symplectic structure can be defined only locally. So it is convenient to describe  $\mathcal{P}_n$  and the reduced (or internal polyad) dynamics under  $\mathcal{H}_n$  within an Euler-Poisson framework using a set of generators of the Poisson algebra of the reduced system.

#### 3. Integrable approximation

The normal form  $\mathcal{H}(q, p)$  and reduced Hamiltonian  $\mathcal{H}_n$  are formal series in the parameter  $\varepsilon$  of the perturbations due to nonlinear terms. Except for the case  $K = 1$  of the diatomic molecule, this series is known to diverge eventually. Nevertheless—and there is the main practical value of the polyad approximation—truncated series  $\mathcal{H}(q, p)$  and  $\mathcal{H}_n$  can give a fair approximation to the original nonintegrable dynamics. Below we will always imply that  $\mathcal{H}(q, p)$  and  $\mathcal{H}_n$  are truncated. Because  $\mathcal{H}(q, p)$  and  $\mathcal{N}(q, p)$  Poisson commute, we call the approximation given by  $\mathcal{H}(q, p)$  *integrable*. This does not mean, of course, that the normalized system is integrable, because the nonintegrability of the internal polyad dynamics with  $K - 1$  degrees of freedom is preserved.

#### 4. Simple examples

Spectroscopists call Hamiltonians  $\mathcal{H}(q, p)$  and  $\mathcal{H}_n$  as *model* (because they rely on the assumption of a certain resonance condition and associated polyad symmetry  $\mathbb{S}^1$ ) and *effective* (because all “non-diagonal” interactions between polyads are accounted for effectively and indirectly). To have a simple example, think of  $K = 2$ . In that case, the space  $\mathcal{P}_n$  is homeomorphic, and for the 1:1 resonance—diffeomorphic to a 2-sphere  $\mathbb{S}^2$ , i.e., the  $\mathbb{C}P^1$  space. The Poisson algebra of the reduced system is similar to the  $\mathfrak{so}(3)$  algebra of the Euler top. The polyad approximation is completely integrable. In the molecular literature (on such molecules as  $\text{H}_2\text{O}$ ,  $\text{O}_3$  and others) [28], the particular case of the two modes in 1:1 resonance has been traditionally called the polyad ap-

TABLE II: Terms in the vibrational Hamiltonian of methane used by Boudon et al. [7]:  $d$  is total degree in vibrational variables,  $\Delta$  is the number of bending-size quanta exchanged by the term,  $\Gamma'_\pm$  and  $\Gamma''_\pm$  and  $\Gamma_\pm = \Gamma$  are intermediate irreducible representations of the  $T_d$  point group used in the tensorial definition by Champion et al. [4, 5]; monomials of  $O(3)$  type  $K$  and degree  $d_i \geq K$  are denoted as  $d_i K \Gamma_i$ , indices of creation-annihilation variables  $a^\dagger$  and  $a$  correspond to normal modes.

Parameter	Value $\text{cm}^{-1}$	$d$	( $\Delta$ )	$\Gamma$	$\Gamma'_+$	$\Gamma''_+$	$a_1^\dagger$	$a_2^\dagger$	$a_3^\dagger$	$a_4^\dagger$	$\Gamma'_-$	$\Gamma''_-$	$a_1$	$a_2$	$a_3$	$a_4$
$\omega_1$	2882.40935	2	(2)	$A_1$	$A_1$	$A_1$	$10A_1$				$A_1$	$A_1$	$10A_1$			
$\omega_2$	1533.33258	2	(1)	$E$	$E$	$E$		$11E$			$E$	$E$		$11E$		
$\omega_3$	2998.45069	2	(2)	$F_2$	$A_1$	$F_2$			$11F_2$		$A_1$	$F_2$			$11F_2$	
$\omega_4$	1310.76161	2	(1)	$F_2$	$A_1$	$A_1$				$11F_2$	$A_1$	$A_1$				$11F_2$
$t_{344}$	-52.17645	3	(2)	$F_2$	$A_1$	$F_2$			$11F_2$		$A_1$	$A_1$				$22F_2$
$t_{324}$	-49.84192	3	(2)	$F_2$	$A_1$	$F_2$			$11F_2$		$E$	$E$		$11E$		$11F_2$
$t_{144}$	100.38526	3	(2)	$A_1$	$A_1$	$A_1$	$10A_1$				$A_1$	$A_1$				$20A_1$
$t_{122}$	7.31404	3	(2)	$A_1$	$A_1$	$A_1$	$10A_1$				$A_1$	$A_1$		$20A_1$		
$t_{4444}$	3.09905	4	(2)	$E$	$A_1$	$A_1$				$22E$	$A_1$	$A_1$				$22E$
$t_{2444}$	0.51881	4	(2)	$F_2$	$E$	$E$		$11E$		$11F_2$	$A_1$	$A_1$				$22F_2$
$t_{2424}$	1.98394	4	(2)	$F_1$	$E$	$E$		$11E$		$11F_2$	$E$	$E$		$11E$		$11F_2$
$t_{2244}^E$	-1.35085	4	(2)	$E$	$E$	$E$		$22E$			$A_1$	$A_1$				$22E$
$t_{2244}^{A_1}$	-10.69933	4	(2)	$A_1$	$A_1$	$A_1$		$20A_1$			$A_1$	$A_1$				$20A_1$
$t_{2222}^E$	-1.52673	4	(2)	$E$	$E$	$E$		$22E$			$E$	$E$		$22E$		
$t_{2222}^{A_1}$	-3.43159	4	(2)	$A_1$	$A_1$	$A_1$		$20A_1$			$A_1$	$A_1$		$20A_1$		
$t_{3434}^{F_2}$	-11.24401	4	(3)	$F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{3434}^{F_1}$	-19.94961	4	(3)	$F_1$	$A_1$	$F_2$			$11F_2$	$11F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{3434}^E$	-19.06810	4	(3)	$E$	$A_1$	$F_2$			$11F_2$	$11F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{3434}^{A_1}$	-33.08916	4	(3)	$A_1$	$A_1$	$F_2$			$11F_2$	$11F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{2334}^{F_2}$	0.21457	4	(3)	$F_2$	$E$	$F_2$		$11E$		$11F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{2334}^{F_1}$	10.95242	4	(3)	$F_1$	$E$	$F_1$		$11E$	$11F_2$		$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{2323}^{F_2}$	-22.58362	4	(3)	$F_2$	$E$	$F_2$		$11E$	$11F_2$		$E$	$F_2$		$11E$	$11F_2$	
$t_{2323}^{F_1}$	-15.55456	4	(3)	$F_1$	$E$	$F_1$		$11E$	$11F_2$		$E$	$F_1$		$11E$	$11F_2$	
$t_{1434}$	14.49813	4	(3)	$F_2$	$A_1$	$A_1$	$10A_1$			$11F_2$	$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{1423}$	34.60149	4	(3)	$F_2$	$A_1$	$A_1$	$10A_1$			$11F_2$	$E$	$F_2$		$11E$	$11F_2$	
$t_{1414}$	-21.44273	4	(3)	$F_2$	$A_1$	$A_1$	$10A_1$			$11F_2$	$A_1$	$A_1$	$10A_1$			$11F_2$
$t_{1234}$	-11.09301	4	(3)	$E$	$E$	$E$	$10A_1$	$11E$			$A_1$	$F_2$			$11F_2$	$11F_2$
$t_{1212}$	-9.67220	4	(3)	$E$	$E$	$E$	$10A_1$	$11E$			$E$	$E$	$10A_1$	$11E$		
$t_{3333}^{F_2}$	-14.26190	4	(4)	$F_2$	$A_1$	$F_2$			$22F_2$		$A_1$	$F_2$			$22F_2$	
$t_{3333}^E$	10.39318	4	(4)	$E$	$A_1$	$E$			$22E$		$A_1$	$E$			$22E$	
$t_{3333}^{A_1}$	-150.42460	4	(4)	$A_1$	$A_1$	$A_1$			$20A_1$		$A_1$	$A_1$			$20A_1$	
$t_{1333}$	-6.31920	4	(4)	$F_2$	$A_1$	$F_2$	$10A_1$		$11F_2$		$A_1$	$F_2$			$22F_2$	
$t_{1313}$	-98.79672	4	(4)	$F_2$	$A_1$	$F_2$	$10A_1$		$11F_2$		$A_1$	$F_2$	$10A_1$		$11F_2$	
$t_{1113}$	-3.15814	4	(4)	$A_1$	$A_1$	$A_1$	$20A_1$				$A_1$	$A_1$			$20A_1$	
$t_{1111}$	-30.25501	4	(4)	$A_1$	$A_1$	$A_1$	$20A_1$				$A_1$	$A_1$	$20A_1$			

proximation [29, 30]. It was used in systems with other resonances [31, 32], such as 2:1:1 in  $\text{CO}_2$  and polyads of acetylene [33–35]. We further extend and develop this concept mathematically. A more substantial review of the relevant work can be found in Refs. [3, 27, 36];

### 5. Quantization and quantum-classical correspondence

From the quantum mechanical point of view, the main advantage of the polyad approximation is that it results in the finite set of basis functions, or more correctly, in working on finite-dimensional subspaces of the Hilbert space. Those of us who think quantum-mechanically see this as block-factorization of the matrix of the original quantum Hamiltonian  $\hat{H}(Q, P)$  resulting from the quantum analogue of the Lie transform normalization techniques called Van-Vleck transformation (see, for example, calculations for methane in Ref. [14]). From the semi-classical perspective, that we take in this work, this is a consequence of the compactness of reduced phase spaces

$\mathcal{P}_n$ .

In comparison to its quantum counterparts [14], classical normalization reproduces only principal terms of quantum commutators. So, strictly speaking, quantization and polyad normalization do not commute. However, for many purposes including ours, corrections arising from the non-principal terms can be neglected. Furthermore, for any spectroscopic purpose, parameters of  $\mathcal{H}_n$  have to be adjusted to reproduce experimental data satisfactorily, and these adjustments are comparable to the quantum corrections we neglect.

The normalized system with Hamiltonian  $\mathcal{H}(q, p)$  can be quantized straightforwardly by replacing  $(q, p)$  for  $(q, -i\hbar\partial/\partial p)$ . The eigenfunctions of the resulting quantum Hamiltonian  $\hat{\mathcal{H}}$  for a given polyad  $n$  can be constructed using oscillator basis functions  $|n_1\rangle|n_2\rangle\cdots|n_K\rangle$  that satisfy

$$\sum_{i=1}^K k_i n_i = n.$$

For a given  $n \gg 1$ , the polyad Hilbert space is spanned by approximately

$$\frac{n^{K-1}}{(k_1 k_2 \cdots k_K)(K-1)!} + O(n^{K-2})$$

functions [37]; the exact number is given by the  $n$ -th degree coefficient of the Taylor expanded generating function

$$g(\lambda) = \prod_{i=1}^K (1 - \lambda^{k_i})^{-1}.$$

The eigenspectrum of  $\hat{\mathcal{H}}$  approximates the energies of the system. The reduced system with Hamiltonian  $\mathcal{H}_n$  can be quantized by replacing generators of its Poisson algebra for appropriate quantum operators [38–40]. In the simple 1:1 example, this gives the standard algebra of angular momentum operators. And of course, for  $K \leq 2$  we can use the EBK quantization principle.

#### 6. Relative equilibria (RE) and internal polyad structure

When the linearized system has degeneracies due to symmetries and resonances, the normal modes reflect little if any dynamics of the system. We should use the *non-linear normal modes* [41–43] instead. These are families of short-period periodic orbits that survive breaking the degeneracy by a system-specific nonlinear perturbation [44, 45]; their number is typically *larger* than  $K$ . Non-linear normal modes can be approximated by lifting non-degenerated stationary points of  $\mathcal{H}_n$  on  $\mathcal{P}_n$  back to the original phase space  $T\mathbb{R}^K$  where they become  $\mathcal{N}$ -orbits of period  $\approx 2\pi/\omega_0$ . So, within the polyad approximation, nonlinear normal modes become *relative equilibria* [66] (RE) of the system.

The importance of RE to the analysis of polyads has been demonstrated repeatedly (see Refs. [3, 27, 43] and references therein). Because RE make up the “skeleton” of a polyad, the study of any polyad system begins with finding and describing its RE for different values  $n$  of the polyad integral  $\mathcal{N}$ . In other words, we consider one-parameter families of RE. As  $n$  increases, this includes uncovering bifurcations, which may, in particular, create new additional RE. The most known example is the creation of *local modes* in  $\text{H}_2\text{O}$ ,  $\text{O}_3$ , and other molecules. Results of the RE analysis can be represented using an energy-momentum diagram (otherwise known as bifurcation diagram) where energies of  $\mathcal{H}_n$  at different RE are displayed as functions of  $n$ . For  $K = 2$  such diagram provides a very detailed characterization of polyads; for large  $K > 2$ , interpreting the RE structure of the polyad becomes more challenging.

## B. Classical description of polyads of methane

The vibrational Hamiltonian of methane is a function of  $K = 9$  vibrational normal mode coordinates  $q$  and corresponding conjugate momenta  $p$ . Our choice of coordinates, numbering of hydrogen atoms, and principal symmetry operations that generate cubic groups are illustrated in Fig. 2. The usual spectroscopic notation is based on the normal mode index  $1 \dots 4$ , the irreducible representation  $\Gamma$  and its row  $\sigma$ , according to which the particular coordinate transforms. We will use complex oscillator variables

$$z = q - ip, \quad \bar{z} = q + ip,$$

which are direct analogs of quantum creation-annihilation operators  $\sqrt{2}a$  and  $\sqrt{2}a^\dagger$  and the following shorthand notation

$z$	mode	$\Gamma$	$\sigma$	$k$	type
$z_1$	$\nu_1$	$A_1$		2	stretching
$z_2$	$\nu_2$	$E$	$a$	1	bending
$z_3$			$b$	1	
$z_4$	$\nu_3$	$F_2$	$x$	2	stretching
$z_5$			$y$	2	
$z_6$			$z$	2	
$z_7$	$\nu_4$	$F_2$	$x$	1	bending
$z_8$			$y$	1	
$z_9$			$z$	1	

where  $k$  indicates the factor in the resonance condition (1).

#### 1. Normalized Hamiltonian $\mathcal{H}$ and reduced Hamiltonian $\mathcal{H}_n$

In the presence of resonance (1), the system can be normalized with regard to the periodic flow of the 9-dimensional harmonic oscillator system with Hamiltonian

$$\mathcal{N}(z) = z_1 \bar{z}_1 + \frac{1}{2} \sum_{i=2}^3 z_i \bar{z}_i + \sum_{i=4}^6 z_i \bar{z}_i + \frac{1}{2} \sum_{i=7}^9 z_i \bar{z}_i. \quad (3)$$

Each  $\mathcal{N}$ -orbit  $\gamma_n$  is a specific simultaneous rotation of symplectic planes  $(z_i, \bar{z}_i)$ ,  $i = 1 \dots 9$ . Starting  $\gamma_n$  at time  $t = 0$  and point  $z = (z_1, z_2, \dots, z_9)$  where  $\mathcal{N}(z) = n$ , we have

$$\gamma_n : z \mapsto (z_1 \theta^2, (z_2, z_3) \theta, (z_4, z_5, z_6) \theta^2, (z_7, z_8, z_9) \theta),$$

where  $\theta = e^{it}$ ,  $\bar{\theta} = e^{-it}$ , and  $t \in [0, 2\pi]$ .

In order to remain invariant along  $\gamma_n$ , the monomials in the normal form  $\mathcal{H}(z, \bar{z})$  should be of certain specific form, e.g.,

$$z_1 \bar{z}_2^2, \quad z_4 \bar{z}_2 \bar{z}_7, \quad \text{etc};$$

they should include such products of  $z$  and  $\bar{z}$  for which the  $\theta$  factors vanish. Further restrictions on the allowed



terms in  $\mathcal{H}(z, \bar{z})$  are imposed by the  $T_d \times \mathcal{T}$  symmetry [3, 4].

There are two ways of arriving at  $\mathcal{H}$ : (i) Similar to Ref. [14], one can take the original vibrational Hamiltonian  $H(Q, P)$  that includes a potential surface  $V(Q)$  and normalize it. (ii) We can take a shortcut and start with the well developed spectroscopic phenomenological rovibrational Hamiltonian  $\mathcal{H}$  of the Dijon group (see Table II, Refs. [7, 8] and references therein). Because  $V(Q)$  of methane is not sufficiently well determined, the second method gives currently more accurate predictions for higher polyads. Furthermore, our purpose is the subsequent analysis based on  $\mathcal{H}$  and the method by which  $\mathcal{H}$  is obtained not important. So we followed the second path. The spectroscopic Hamiltonian  $\mathcal{H}$  in Table II is already in normal form but its terms are defined implicitly using the Wigner-Eckart theorem and various coefficients [4]. Explicit expressions for the Hamiltonian used in Refs. [7, 8], such as the ones in Ref. [27], can be obtained by a careful analysis of definitions in Ref. [4]. Thus we get the quadratic part

$$\mathcal{H}^0 = \frac{\omega_1}{2} z_1 \bar{z}_1 + \frac{\omega_2}{2} \sum_{i=2}^3 z_i \bar{z}_i + \frac{\omega_3}{2} \sum_{i=4}^6 z_i \bar{z}_i + \frac{\omega_4}{2} \sum_{i=7}^9 z_i \bar{z}_i,$$

and the cubic part

$$\begin{aligned} \mathcal{H}^1 = & -\frac{t_{144}}{4\sqrt{3}} z_1 (\bar{z}_7^2 + \bar{z}_8^2 + \bar{z}_9^2) - \frac{t_{122}}{4\sqrt{2}} z_1 (\bar{z}_2^2 + \bar{z}_3^2) \\ & + \frac{t_{344}}{2\sqrt{2}} (z_4 \bar{z}_8 \bar{z}_9 + z_5 \bar{z}_7 \bar{z}_9 + z_6 \bar{z}_7 \bar{z}_8) \\ & + \frac{t_{324}}{4\sqrt{2}} z_2 (\bar{z}_4 z_7 + \bar{z}_5 z_8 - 2\bar{z}_6 z_9) \\ & - \frac{t_{324}}{4\sqrt{2}} \sqrt{3} z_3 (\bar{z}_4 z_7 - \bar{z}_5 z_8) \\ & + \text{c.c.} \end{aligned}$$

In the present work, we went up to the quartic terms; their expressions are lengthy and we do not provide them here.

To reduce the normalized system with Hamiltonian  $\mathcal{H}(z, \bar{z})$  we first construct and describe the reduced phase space  $\mathcal{P}_n$  as a (possibly singular) Poisson manifold using a certain number of polynomial generators of the Poisson algebra of the reduced system. Then we rewrite  $\mathcal{H}(z, \bar{z})$  so that it becomes a function  $\mathcal{H}_n$  of the above generators, in other words, a function on  $\mathcal{P}_n$ , and parameter  $n$ . For polyads with  $K - 1 = 8$  internal degrees of freedom, the latter operation is, however, hardly advantageous because the generator basis is large and is complicated by syzygies. So instead we will use appropriate  $\mathbb{C}^8$  charts of  $\mathcal{P}_n$  and work essentially with  $\mathcal{H}(z, \bar{z})$  projected in the charts. See Refs. [3, 27, 46] for key technical aspects and the following section.

## 2. Projective decomposition of the reduced phase space $\mathcal{P}_n$

Reduced Hamiltonian  $\mathcal{H}_n$  is a function on the polyad space  $\mathcal{P}_n$  of real dimension  $8 \times 2$ . Points of  $\mathcal{P}_n$  can be described using complex variables  $z$  by the method outlined in Ref. [27]. Following [27], we *decompose* the large polyad space in terms of several polyad subspaces or *polyad projections*. Each projection is itself a polyad space of a smaller system. Thus the  $\nu_2$  projection is a polyad space of isolated  $\nu_2$  polyads, i.e., of a system of two oscillators in 1:1 resonance (with a specific  $C_{3v}$  symmetric perturbation similar to that in the Hénon–Heiles potential). It is, therefore, a  $\mathbb{C}P^1 \sim \mathbb{S}^2$  [3]. Similarly, both the  $\nu_3$  and the  $\nu_4$  projections have  $\mathbb{C}P^2$  topology. We combine projections by introducing *mixing coordinates* for amplitude  $\eta \in [0, 1]$  and phase and  $\phi \in [0, 2\pi)$ . Specifically, we write

$$z = \sqrt{n} \begin{pmatrix} \sqrt{\eta_1} \exp(i\phi_1) \zeta_1, \\ \sqrt{2\eta_2} \exp(i\phi_2) (\zeta_2, \zeta_3), \\ \sqrt{1 - \eta_1 - \eta_2 - \eta_4} (\zeta_4, \zeta_5, \zeta_6), \\ \sqrt{2\eta_4} \exp(i\phi_4) (\zeta_7, \zeta_8, \zeta_9) \end{pmatrix}, \quad (4)$$

where  $\zeta_1 \equiv 1$  for  $\nu_1$ , and unimodular vectors  $(\zeta_2, \zeta_3)$ ,  $(\zeta_4, \zeta_5, \zeta_6)$ , and  $(\zeta_7, \zeta_8, \zeta_9)$  define points on the respective  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  polyad projections. Note that the space described by coordinates  $(\zeta, \phi)$  is itself a projective space. Substituting in (3), we can verify that  $\mathcal{N}(z) = n$  for any  $z$  defined by (4). The simplest two-mode mixing case of stretching modes  $\nu_1$  and  $\nu_3$  ( $K = 4$ ) which required one pair of mixing coordinates  $(\eta_1, \phi_1)$  was studied in Ref. [27]. In the general case of Eq. (4), we should use six such coordinates to mix all four normal modes. Also note that Eq. (4) implies that  $\eta_1 + \eta_2 + \eta_4 < 1$ , i.e., that the  $\nu_3$  contribution is non-zero. Furthermore, this form is most efficient when  $\eta_1 + \eta_2 + \eta_4 \ll 1$ . Such representation is called a  $\nu_3$ -*chart* of  $\mathcal{P}_n$ .

TABLE III: Representatives of isolated fixed points of the  $T_d \times \mathcal{T}$  group action on the  $\nu_3$  and  $\nu_4$  polyad subspaces  $\mathbb{C}P^2$ , the  $\nu_2$  subspace  $\mathbb{C}P^1$  and on the rotational sphere  $\mathbb{S}^2$  [3]. For each representative, we indicate the class of conjugated subgroups of  $T_d \times \mathcal{T}$  of its stabilizer, and give in parentheses the number of equivalent points with stabilizer in the same class.

Stabilizer		$\mathbb{C}P^1$		$\mathbb{C}P^2$			$\mathbb{S}^2$			
		$\zeta_2$	$\zeta_3$	$\zeta_{4,7}$	$\zeta_{5,8}$	$\zeta_{6,9}$	$j_1$	$j_2$	$j_3$	
$D_{2d} \times \mathcal{T}$	(3)	1	0	1	0	0	0	1	0	0
$C_{3v} \times \mathcal{T}$	(4)	$b$	$ib$	$a$	$a$	$a$	$a$	$a$	$a$	$a$
$C_{2v} \times \mathcal{T}$	(6)	1	0	$b$	$b$	0	$b$	$b$	0	0
$S_4 \wedge \mathcal{T}_2$	(6)	1	0	$b$	$ib$	0	1	0	0	0
$C_3 \wedge \mathcal{T}_s$	(8)	$b$	$ib$	$a$	$\chi^2 a$	$\chi a$	$a$	$a$	$a$	$a$

Here  $a = 1/\sqrt{3}$ ,  $b = 1/\sqrt{2}$ ,  $\chi = e^{i\pi/3}$ .

### 3. Relative equilibria (RE)

In our case, a general search for RE is a formidable task that requires finding stationary points of function  $\mathcal{H}_n$  (equilibria) on a curved compact space  $\mathcal{P}_n$  of real dimension 16. We should first exploit fully the symmetry group  $T_d \times \mathcal{T}$  of our system. Specifically,  $T_d \times \mathcal{T}$  acts on  $\mathcal{P}_n$  in such a way that  $\mathcal{P}_n$  becomes stratified in various low-dimensional subspaces that are invariant with respect to subgroups  $G \subseteq T_d \times \mathcal{T}$ , called *stabilizers* or *isotropy groups*. For a  $G$ -isotropic subspace, all non-vanishing components of  $\nabla \mathcal{H}_n$  should be tangent to it, and if  $G$  is symplectic, the dynamics may be restricted to it as well. Obviously, the search for possible particular solutions becomes easier with decreasing dimension.

We can argue using the principles of Morse theory [47] that among all RE, there must be a number of RE that are invariant with regard to different stabilizers  $G \subseteq T_d \times \mathcal{T}$ . In the simple “minimal” cases, in particular at low  $n$ , our  $\mathcal{H}_n$  may have only symmetric stationary points with sufficiently large stabilizers  $G$  whose existence is caused primarily by the action of the symmetry group  $T_d \times \mathcal{T}$  and the topology of  $\mathcal{P}_n$  [47]. These RE are much easier to find as stationary points of  $\mathcal{H}_n$  on  $\mathcal{P}_n$  (because several equations in  $\nabla \mathcal{H}_n = 0$  are satisfied automatically due to symmetry). They correspond to points of  $\mathcal{P}_n$  that belong to specific non-generic orbits of the  $T_d \times \mathcal{T}$  action. The set of all orbits of the same type form a *stratum*. The topology of the system of strata, and specifically, the presence of low-dimensional isolated components within a stratum and within this system is of prime importance here. In the simplest case, we may find isolated points that represent *critical* orbits. Points on such orbits are *necessarily*  $G$ -invariant stationary points of  $\mathcal{H}_n$  [47].

We turn to studying how  $T_d \times \mathcal{T}$  acts on our 16-dimensional  $\mathcal{P}_n$ . The dimension of  $\mathcal{P}_n$  is too high for critical orbits to occur, instead we have “small” isolated  $G$ -invariant subspaces of  $\mathcal{P}_n$  [67]. We like to find  $G$ -invariant subspaces  $\mathcal{P}_n^G \subset \mathcal{P}_n$  with smallest possible dimension. Such subspaces will be called *minimal fixed spaces* of the  $T_d \times \mathcal{T}$  action on  $\mathcal{P}_n$ .

In order to find minimal  $G$ -invariant subspaces  $\mathcal{P}_n^G$ , we take advantage of our decomposition of  $\mathcal{P}_n$  in Eq. (4). We study the action of  $T_d \times \mathcal{T}$  on each of the polyad projections of  $\mathcal{P}_n$ , namely the  $\mathbb{C}P^1 \sim \mathbb{S}^2$  space of isolated  $\nu_2$ -polyads, the  $\mathbb{C}P^2$  space of isolated  $\nu_3$ -polyads. On all these spaces, the action of  $T_d \times \mathcal{T}$  has critical orbits [3, 46]. So it follows that  $\mathcal{P}_n^G$  is minimal if in each projection it is represented by a fixed point on the critical orbit of the  $T_d \times \mathcal{T}$  action on this projection. When all modes are present (i.e., if neither of the amplitude mixing coordinates  $\eta$  is 0), we can deduce from Eq. (4) that minimal fixed spaces are 2:1:2:1 weighted projective spaces of real dimension 6. Fixed points in the  $\mathbb{C}P$  projections were determined in Ref. [3, 46] for all possible stabilizers  $G$ . We list them in Table III. We also give the corresponding fixed points  $(j_1, j_2, j_3)$  on the rotational sphere

$\mathbb{S}^2$  to allow extending the analysis to rotation-vibration Hamiltonians  $\mathcal{H}(z, \bar{z}, j)$ , but for now we assume no rotation ( $j = 0$ ) for simplicity.

Using information in Table III requires basic understanding of the  $T_d \times \mathcal{T}$  action on projective spaces. The idea is to substitute coordinates  $\zeta$  in Eq. (4) for the ones in this table and allow for mixing coordinates  $(\eta, \phi)$  to vary. However, this will not always preserve the isotropy because  $G \subseteq T_d \times \mathcal{T}$  may act nontrivially on the phase mixing coordinates  $\phi$  and produce nontrivial automorphisms  $\mathcal{P}_n^G \leftrightarrow$ . As a result, the actual stabilizers  $\tilde{G} \subseteq G$  of points of  $\mathcal{P}_n^G$  may be lower and  $\mathcal{P}_n^G$  may contain lower dimensional strata of points with nontrivial isotropy. So in general,  $G$  refers to the symmetry of the projections of  $\mathcal{P}_n^G$  and not to the actual stabilizer of its points. For this reason we will call  $G$  *projected stabilizer*.

For example [27], from Eq. (4) with  $\eta_2 = \eta_4 = 0$  we can see that  $\mathcal{T} : z \mapsto \bar{z}$  acts on purely stretching subspaces as  $\phi_1 \mapsto -\phi_1$ . In fact [27], purely stretching symmetry preserving normal mode mixing is only allowed for the two topmost stabilizers in Table III which we will call for brevity  $D_{2d}$  and  $C_{3v}$ . Of course, mixing is always possible for generic RE that appear eventually with growing  $n$  as the dynamics becomes increasingly irregular, but mixing possibilities at low  $n$  seem to be quite limited.

This remarkable result is little known, and its full value remains to be uncovered. Because we are interested primarily in mixing, we focus in Sec. III C below on RE of these two types. Other symmetric RE, though non-linear in nature, are of non-mixed normal mode content and are likely (as in the case studied in Ref. [27]) to be unstable.

### C. Symmetric stretching relative equilibria

Now we can find RE as symmetric stationary points of  $\mathcal{H}_n$ . For all possible stabilizers  $G \subseteq T_d \times \mathcal{T}$ , we restrict  $\mathcal{H}_n$  on minimal fixed spaces  $\mathcal{P}_n^G$  and search for stationary points of the restricted function  $\mathcal{H}_n|_{\mathcal{P}_n^G} : \mathcal{P}_n^G \rightarrow \mathbb{R}$ . The search can be further simplified by taking the stratification of  $\mathcal{P}_n^G$  into account. Note also that polar coordinates  $(\eta, \phi)$  do not reflect correctly the geometry of  $\mathcal{P}_n^G$  and should be used with usual precautions at ‘poles’  $\eta = 0$  and  $\eta = 1$ . Ideally, one should analyze the whole family of vibrational polyad RE of methane (and extend them to rotational-vibrational RE). This, however, is not immediately feasible here. Our approach is relatively new and we like to develop it more fully on a small number of examples. So we restrict the analysis to a few potentially most important RE.

We turn here to stabilizers  $C_{3v}$  and  $D_{2d}$  because they allow normal mode mixing and because such highly symmetric RE are more likely to remain elliptic. Additionally, we will neglect bending contributions, assuming  $\eta_2 = \eta_4 = 0$ . This has two aspects. One of the  $C_{3v}$  RE is smoothly related [27] to what spectroscopists call local mode [10, 12, 23–26]. Local modes are well pronounced in certain molecules and we like to clarify the situation in

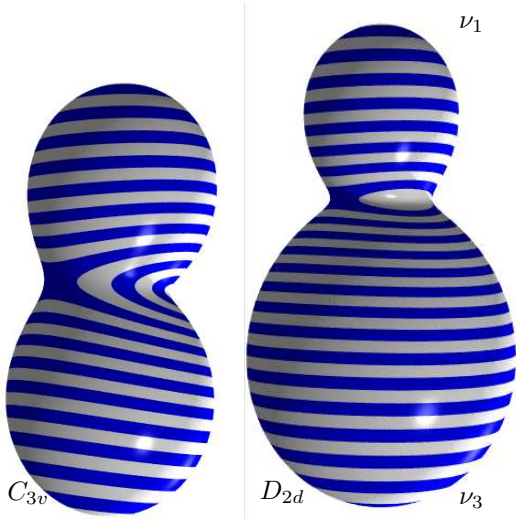


FIG. 7: Coupling surfaces of stretching ( $\nu_1, \nu_3$ ) relative equilibria of methane with isotropy  $C_{3v}$  (left) and  $D_{2d}$  (right) for polyad  $P_8$ . The surfaces are stripe painted at fixed equidistant energy intervals; pure  $\nu_1$  and  $\nu_3$  are at  $\phi = 0$  (North) and  $\phi = \pi$  (South) poles. The  $D_{2d}$  surface has a vertical symmetry axis  $C_2$  while the  $C_{3v}$  one does not; the latter has no stationary point exactly at  $\phi = \pi$ .

methane. At the same time, we also like to minimize the theory required for understanding our particular experimental results. Because of the 2:1 stretching-to-bending frequency ratio, absorbing stretching vibrational quanta is the “shortest” way to reach highly excited polyads. In the Taylor series for the effective polyad transition moment  $\mu_{\text{eff}}$  (see Sec. IV), the lowest degree terms describing the  $P_0 \rightarrow P_n$  transition are of maximal degree  $\approx n/2$  in stretching variables ( $z_1, z_4, z_5, z_6$ ). Intensity depends both on the coefficient in the  $\mu_{\text{eff}}$  series and the upper state wavefunction. So it makes sense to investigate whether absorption can be channeled in a predominantly stretching localized vibration.

### 1. The $C_{3v}$ RE

Substituting subsequently  $z$  in Eq. (4) and  $\zeta$  for stabilizer  $C_{3v} \times \mathcal{T}$  in Table III into  $\mathcal{H}(z) = \mathcal{H}^0(z) + \mathcal{H}^1(z) + \mathcal{H}^2(z)$  described in Sec. III B, we obtain a function  $\mathcal{H}_n^{C_{3v}}(\eta, \phi)$ , where in the  $\nu_3$ -chart we have  $\eta = (\eta_1, \eta_2, \eta_4)$  and similarly  $\phi = (\phi_1, \phi_2, \phi_4)$ .  $\mathcal{H}_n^{C_{3v}}(\eta, \phi)$  lives on the mixing space of real dimension 6. Fixing  $\eta \equiv (\eta_1, 0, 0)$ , we project  $\mathcal{H}_n^{C_{3v}}(\eta, \phi)$  on an  $\mathbb{S}^2$  subspace with cylindrical coordinates  $(\eta_1, \phi_1)$ . This is the simplest mixing space [27]. Points of this space represent different phase and amplitude combinations of the two stretching modes  $\nu_1$  and  $\nu_3$  with projected stabilizer  $C_{3v} \times \mathcal{T}$ . The coupling space  $\mathbb{S}^2$  is cut into two halves by the above mentioned action of  $\mathcal{T}$ . The respective reflection plane  $\{\phi_1 = 0, \pi\}$  intersects  $\mathbb{S}^2$  on a circle  $\mathbb{S}^1$  of  $C_{3v} \times \mathcal{T}$ -invariant points with one exceptional  $T_d \times \mathcal{T}$ -invariant fixed point  $\nu_1$ . All

other points have isotropy  $C_{3v}$ . Defining longitude and latitude angles  $\theta \in [0, \pi]$  and  $\phi \in [0, 2\pi)$  so that

$$\eta_1 = (1 + \cos \theta)/2, \quad \text{and} \quad \phi_1 = \phi,$$

and using the values of parameters in Table II we obtain

$$\begin{aligned} \mathcal{H}_n^{C_{3v}} = & \mathcal{H}' + \mathcal{H}'' - 0.45605 n^2 \sin \theta (1 - \cos \theta) \cos \phi \\ & + (3.47924 \cos^2 \theta + 1.83715 \cos \theta - 9.0983) n^2, \end{aligned}$$

where

$$\begin{aligned} \mathcal{H}' &= (48.1679 - 29.0103 \cos \theta) n, \\ \mathcal{H}'' &= (0.22792 \sin^2 \theta \cos^2 \phi) n^2. \end{aligned}$$

This function is depicted in Fig. 7 for  $n = 8$ . We can see that it has a maximum at the North pole (pure  $\nu_1$ ), a similar high maximum near the South pole, and a shallow minimum-saddle pair in the ravine at  $\eta_1 \approx 1/2$  (near 50% mixing). All these critical points on  $\mathbb{S}^2$  correspond to different stretching  $C_{3v}$  RE. Finding them has been described in more detail in Ref. [27]. We notice that the Hamiltonian  $\mathcal{H}_n^{C_{3v}}$  is  $\mathcal{T}$ -invariant and is therefore symmetric with respect to the reflections  $\phi \mapsto -\phi$ .

All stationary points that we have found lie on the  $\mathcal{T}$ -circle. The *fixed* point at the North pole represents 100% pure  $\nu_1$  mode. The point near the South pole is not fixed; it can move on  $\mathbb{S}^1$ , but it does it only slightly, and the respective RE remains very close to pure  $\nu_3$ . This is very different from the local mode scenario [27] where this RE evolves smoothly into the local mode with  $\approx 30\%$   $\nu_1$  content. The two other stationary points represent additional strongly mixed stretching RE; they appear as a result of a bifurcation of the  $\nu_1$  RE, see Sec. III C 3.

For the purposes of our later analysis, it is instructive to look more closely at the near South pole RE. Since it is almost pure  $\nu_3$ , it can be characterized sufficiently well by the invariant variables

$k$	$n_{3,k}$	$s_{3,k}$	$t_{3,k}$
1	$(z_4 \bar{z}_4)/2$	$(z_5 \bar{z}_6 + z_6 \bar{z}_5)/2$	$(z_5 \bar{z}_6 - z_6 \bar{z}_5)i/2$
2	$(z_5 \bar{z}_5)/2$	$(z_4 \bar{z}_6 + z_6 \bar{z}_4)/2$	$(z_6 \bar{z}_4 - z_4 \bar{z}_6)i/2$
3	$(z_6 \bar{z}_6)/2$	$(z_4 \bar{z}_5 + z_5 \bar{z}_4)/2$	$(z_4 \bar{z}_5 - z_5 \bar{z}_4)i/2$

describing the internal polyad dynamics on the  $\nu_3$  subspace  $\mathbb{C}P^2 \subset \mathcal{P}_n$ , cf Table 21 and 31 of Ref. [3]. Notice that vector  $t_3 = (t_{3,1}, t_{3,2}, t_{3,3})$  represents the angular momentum induced by the  $\nu_3$  vibrations. Using Eq. (4) and the  $C_{3v} \times \mathcal{T}$  entry in Table III, we obtain that  $n_{3,k} \approx n/6$ ,  $s_{3,k} \approx n/3$ , and  $t_3 = 0$ . So it follows that quantum states localized near such RE should have very low (in comparison to the polyad number  $n$ ) vibrational angular momentum.

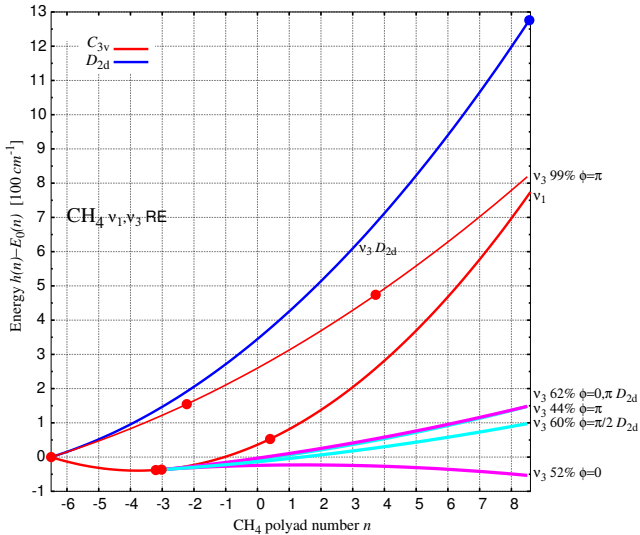


FIG. 8: Energy of stretching  $(\nu_1, \nu_3)$  relative equilibria of methane as a function of polyad quantum number  $n$ . Circles mark bifurcations. Negative values of  $n$  correspond to classically allowed values  $n + 6\frac{1}{2}$  of the polyad integral  $\mathcal{N} \geq 0$ .

## 2. The $D_{2d}$ RE

Choosing the  $D_{2d} \times \mathcal{T}$  entry in Table III and following the same approach as in the previous section, we obtain

$$\mathcal{H}_n^{D_{2d}} = \mathcal{H}' + \mathcal{H}'' + (3.99289 \cos^2 \theta + 0.80985 \cos \theta - 8.5846) n^2,$$

which is simpler than  $\mathcal{H}_n^{C_{3v}}$ . The reason is that the the image of  $D_{2d} \times \mathcal{T}$  acting on the  $D_{2d}$  coupling sphere  $\mathbb{S}^2$  is an abstract symmetry group is  $D_2 = \mathbb{Z}_2 \times \mathcal{T}$ , where the additional  $\mathbb{Z}_2$  corresponds to the  $C_2$  rotations about axes orthogonal to the  $S_4$  axis and acts as  $\phi \mapsto \phi + \pi$ . This produces on  $\mathbb{S}^2$  the spatial group  $C_{2v}$  with reflections in planes  $\phi = 0, \pi$  and  $\phi = \pm\pi/2$  and  $C_2$  rotations about axis  $\nu_1\nu_3$ , under which the Hamiltonian  $\mathcal{H}_n^{D_{2d}}$  is invariant. We depicted  $\mathcal{H}_n^{D_{2d}}$  with  $n = 8$  in Fig. 7, right. Its stationary points lie on the symmetry strata: at the poles and in the planes. Both poles (on the rotation axis) are fixed points, they represent 100% pure  $\nu_1$  and  $\nu_3$ . Points in the planes come in pairs and can move (pairwise) in one dimension when  $n$  is changed; they are created in the bifurcations of the  $\nu_1$  RE described Sec. III C 3.

## 3. Bifurcations involving the $C_{3v}$ and $D_{2d}$ RE

We follow briefly the modifications that the stretching  $C_{3v}$  and  $D_{2d}$  RE families undergo with growing value  $n + 6\frac{1}{2} > 0$  of the classical polyad integral  $\mathcal{N}$  [68]. In this context, Fig. 8 showing energies of stretching RE versus  $n$  serves as a bifurcation diagram. We notice first the characteristic qualitative deformation resulting from

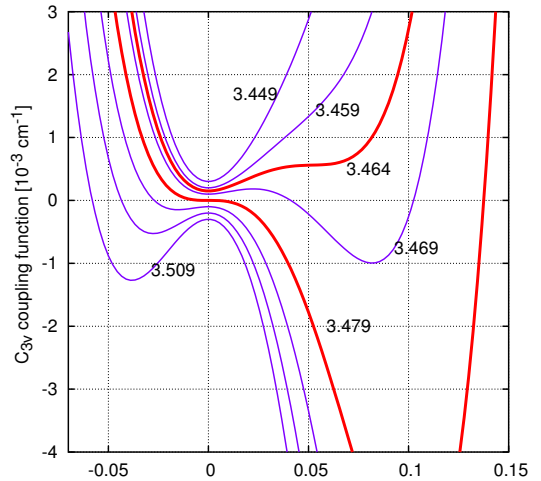


FIG. 9:  $C_{3v}$  coupling function for stretching modes  $(\nu_1, \nu_3)$  of methane near the  $\nu_1$  RE ( $x = 0$ ) for different values  $n + 6\frac{1}{2}$  of polyad integral  $\mathcal{N}$  and  $y = 0$  ( $\phi = 0, \pi$ ). Each curve is shifted vertically for better comparison; bolder lines mark critical sections.

a series of closely succeeding bifurcations of the  $\nu_1$  RE near  $\mathcal{N} \approx 3$ . Like the local-mode-creating bifurcation in simpler systems ( $\text{H}_2\text{O}$ ,  $\text{SiH}_4$ ), this event takes place at very small  $\mathcal{N}$ , below the energy of the ground state, as a result of strong coupling between  $\nu_1$  and  $\nu_3$ .

The smallest possible number of stationary points that a Morse function  $\mathcal{H}_n^\Gamma$  can have on  $\mathbb{S}^2$  is two, a minimum and a maximum. When  $\mathcal{N} < 3$ , both  $C_{3v}$  and  $D_{2d}$  coupling functions are of this simplest kind, with minimum at  $\nu_1$  and maximum at  $\nu_3$ . We can say that the system is essentially uncoupled. Since the number of different  $C_{3v}$  and  $D_{2d}$  stabilizers is 4 and 3, respectively, the total number of stretching RE with these projected stabilizers is 8. (Think of four  $C_{3v}$  and three  $D_{2d}$  coupling spheres  $\mathbb{S}^2$  all sharing their  $\nu_1$  poles; see Refs. [3, 41, 42] for details on counting the total number of nonlinear normal modes of methane.)

The first bifurcation occurs on the  $D_{2d}$  sphere at  $\mathcal{N} \approx 3.298$ . It is a pitchfork bifurcation with broken symmetry of order 2. The  $\nu_1$  RE goes unstable (on this sphere) and a pair of new stable  $D_{2d}$  RE with  $\phi = \pm\pi/2$  are emanated. As  $n$  increases, the pair descends South and takes more  $\nu_3$  content. Next we have a saddle-node bifurcation that takes place on the  $\phi = 0$  semicircle of the  $C_{3v}$  sphere very close to the minimum at the  $\nu_1$  pole. It creates a new minimum which moves away from the pole (thus gaining  $\nu_3$  content) and a saddle that moves towards the pole. What happens can be best observed projecting the coupling sphere in the  $\mathbb{R}^2$  plane tangent at the  $\nu_1$  pole with coordinates

$$(x, y) = \frac{1}{2} \sin \theta (\cos \phi, \sin \phi),$$

such that

$$\cos \theta = \sqrt{1 - 4(x^2 - y^2)}.$$

Additionally, since the reflection symmetry is not broken, we can fix  $y = 0$ , and study the dependence of  $\mathcal{H}_n^{C_{3v}}$  on  $x$  and parameter  $n$  as illustrated in Fig. 9.

The deformation culminates in a more complex event at  $\mathcal{N} = 3.478$  that creates two new unstable RE with  $\phi = 0, \pi$  on the  $D_{2d}$  sphere, while at the same time, the saddle on the  $C_{3v}$  sphere moves through the  $\nu_1$  pole to the  $\phi = \pi$  semicircle while the pole turns into a maximum, see Fig. 9. So we end up with coupling surfaces in Fig. 7. At sufficiently large  $n$ , all newly created RE have minimum energies, while the “original”  $\nu_1$  and  $\nu_3$  RE evolve towards maximal energies arriving for  $n = 8$  at the energy gap of 500–1000  $\text{cm}^{-1}$ , see Fig. 8. This is comparable to the local-mode well in  $\text{SiH}_4$  [27].

Finally, we like to mention a number of bifurcations of these original stretching RE which involve bending modes and change the full 8-degree-of-freedom stability (see respective circles in Fig. 8). In particular, very early at  $\mathcal{N} = 4.272$ , the  $C_{3v}$   $\nu_3$  RE goes through a Hopf bifurcation involving both  $\nu_2$  and  $\nu_4$ ; later at  $\mathcal{N} = 10.224$ , this RE has a pitchfork bifurcation that involves  $\nu_4$ . This indicates very clearly that stretching-bending distinction is not globally valid in methane and that the information we acquired in this section on the stretching RE remains incomplete.

#### 4. Dipole active localization

Ignoring bending degrees of freedom, we can, nevertheless, suggest certain localization possibilities and select the ones that induce the largest dipole moment. We consider stable (in the restricted sense) stretching RE. For  $n = 8$ , all original stretching RE, are stable and furthermore, we have stable RE amongst newly created ones at bottom energies. We notice immediately, that the  $\nu_1$  RE and the  $D_{2d}$   $\nu_3$  RE (maximum energy in Fig. 8) cannot induce any dipole moment. At the same time, because of the shallow valley geometry of the coupling surfaces (Fig. 7), stretching localization near one of the new low-energy RE is incomplete; it resembles that of a hindered one-dimensional rotor. It follows that the most simple candidate to explore below in Sec. IV is the  $C_{3v}$  ( $\phi = \pi$ )  $\nu_3$  RE. We further note that (in polyads  $P_2$  and  $P_4$ ) the overtones of  $\nu_3$  are known to be the states with strongest absorption, and that motion along the  $C_{3v}$  RE results in the most significant electric dipole moment oscillations.

We like to remind here (cf Fig. 16 of Ref. [3] for  $C_{3v} \times \mathcal{T}$ ) that unlike the  $\nu_1$  RE and the  $D_{2d}$   $\nu_3$  RE, which are essentially just normal modes  $\nu_1$  and  $\nu_3$ , the  $C_{3v}$   $\nu_3$  RE is a specific nonlinear normal mode with zero angular momentum. In the configuration space  $\mathbb{R}^3$  of the normal  $\nu_3$  displacements, it corresponds to vibrations along one of the four  $C_3$  axes of the tetrahedron. As a consequence, the respective localized state is four times (quasi)degenerate, just as the local mode to which this RE is smoothly connected.

## IV. INTENSITY OF SINGLE PHOTON TRANSITIONS $P_0 \rightarrow P_n$ WITH LARGE $n$

In this section, we consider the description of the intensity of the direct transition  $P_0 \rightarrow P_n$ , and in particular, we like to understand its dependence on the polyad number  $n$ . For sufficiently large  $n$ , this can be done semi-classically.

We pursue two approaches. In the model approach, we try to reduce the analysis to a single dimension corresponding to the polyad degree of freedom. We select a predominant direction of the dipole active distortion of the molecule along a stable RE. Following Sec. III C 4, we focus on the  $C_{3v}$  RE. In a more general approach, we investigate the possibility to rewrite the dipole moment operator in such a way that the polyad degree of freedom becomes separated.

We also explore the origins of the terms in the polyad dipole moment. Using the normalizing transformation  $(Q, P) \mapsto (q, p)$  introduced in Sec. III A, we express the original vibrationally induced (oscillating) dipole moment  $\mu(Q)$  in the variables  $(q, p)$  of the normalized system and obtain the *effective dipole moment*  $\mu_{\text{eff}}(q, p)$ . For the quantized normalized system, neglecting rotation of the molecule and assuming that the electric field component of the radiation  $\mathbf{E}$  and dipole moment  $\boldsymbol{\mu}$  are collinear, the probability of the transition  $|0\rangle \rightarrow |n\rangle$  is proportional to  $|\langle 0 | \hat{\mu}_{\text{eff}}(q, p) | n \rangle|^2$ .

### A. One-dimensional Morse oscillator model

The general scheme can be illustrated using a one-dimensional Morse oscillator with Hamiltonian

$$H_{\text{Morse}} = \frac{p_r^2}{2M} + D_e \left[ 1 - \exp\left(-\alpha \frac{r - r_e}{r_e}\right) \right]^2,$$

where parameters  $D_e$ ,  $r_e$ , and  $\alpha$ , represent the dissociation energy, the equilibrium distance, and the “strength” of the chemical bond, and  $M$  is the reduced mass. The Birkhoff normal form for this system

$$\mathcal{H} = \omega_0 (N - 2\varepsilon^2 N^2) \quad (5a)$$

is a polynomial of degree 2 [69] in the classical action

$$N = \frac{1}{2}(p^2 + q^2) \quad (5b)$$

with the smallness parameter

$$\varepsilon = \frac{1}{2} \sqrt{\alpha/r_e} (2D_e M)^{-1/4} \quad (5c)$$

and the frequency

$$\omega_0 = 8D_e \varepsilon^2 \quad (5d)$$

of harmonic oscillations about the equilibrium  $r = r_e$ . Taylor expanding the canonical transformation that brings the system to this normal form gives for  $Q = r - r_e$

$$Q \mapsto 2\varepsilon \frac{r_e}{\alpha} \left( q + \varepsilon (q^2 + 2p^2) + \frac{\varepsilon^2}{2} (5q^2/3 - p^2) q + \dots \right).$$

Rewriting the first (linear) term of the vibrationally induced dipole moment  $\mu(Q) = \mu_1 Q + \dots$ , in terms of the dynamical variables  $(q, p)$  of the normalized system, and quantizing the latter, we compute the matrix element

$$\langle 0 | \mu_{\text{eff}} | n \rangle = \mu_1 \frac{r_e}{\alpha} \varepsilon^n (-1)^{n-1} \frac{\sqrt{2^n n!}}{n} \quad (6)$$

that describes the transition  $|0\rangle \rightarrow |n\rangle$ .

### B. Generalization to the multi-dimensional case

The motion along the classical  $S^1$  orbits defined by the polyad integral  $\mathcal{N}$  can be associated with a 1D anharmonic oscillator system, such as the Morse oscillator in Sec. IV A. If this motion corresponds to an RE and the latter is an elliptic orbit stable enough for quantum localization to occur, the induced dipole moment for the localized states will be defined primarily by the deformations of the molecule associated to the particular classical RE. The system becomes, therefore, essentially one-dimensional and we can use the results of the previous section, namely Eq. (6) with  $n$  treated as the value of  $\mathcal{N}$ .

Polyads of the  $\text{CH}_4$  molecule were approximated globally in Ref. [48] using a one-dimensional Morse oscillator with frequency which is naturally close to that of bending vibrations ( $1582 \text{ cm}^{-1}$  for  $\nu_2$  and  $1367 \text{ cm}^{-1}$  for  $\nu_4$  [49]). However, the 1:2 resonance makes the situation singular. Because of the resonance, any purely stretching RE is “short”, i.e., its frequency  $\omega_0$  is twice that of the  $\mathcal{N}$  motion. Furthermore, if we double the polyad frequency when working with such an RE, then in Eq. (6) we should also use the number of stretching quanta  $n/2$  instead of the polyad number  $n$ . For the  $C_{3v} \times T \nu_3$  RE of the  $\text{CH}_4$  molecule we can use the following values (in  $\text{cm}^{-1}$ , atomic units, and Debye)

$$\begin{aligned} \mu_1 & 0.352 [50], 0.390 [49] \text{ D}/a_0 \text{ (for } \nu_3), \\ D_e & 35000 [9] \text{ or } 37360 [48] \text{ cm}^{-1}, \\ \omega_0 & 2 \times 1563.6 [48] \text{ or } 3095 [49] \text{ cm}^{-1}, \\ \varepsilon & \approx 0.10 \text{ (from } D_e, \text{ and } \omega_0), \\ f & 0.332 E_h/a_0^2 (\nu_3 \text{ force constant) [49], \\ M & 0.916 m_u \text{ (from } f/\omega_0^2), \\ r_e/\alpha & 1.0 a_0 \text{ (from } \varepsilon, D_e, \text{ and } M), \end{aligned}$$

and obtain from Eq. (6) the vibrational transition moment  $|\langle \mu \rangle| = |\langle 0 | \hat{\mu}_{\text{eff}}(q, p) | n/2 \rangle|$  for the  $0 \rightarrow P_n$  transitions (see Table VI). Below we use these values to give estimates of the intensity of the most prominent lines in the rotationally resolved  $0 \rightarrow P_n$  bands with  $n = 8, 10, 12$ .

The cross-section for a single absorption line

$$\sigma(\nu) = 2\pi^2 |\langle \mu \rangle|^2 (3\eta \varepsilon_0 c h)^{-1} F(T, J) \nu g(\nu - \nu_0)$$

includes dielectric constant  $\eta \approx 1$ , line form-factor  $g(\nu - \nu_0)$ , and factor  $F(T, J)$  that accounts for the population of the lower state with a given angular momentum  $J$ , degeneracy of that state, and rotational matrix elements.

TABLE VI: Estimated absorption cross-sections  $\sigma$  of the most intense rotational transitions in the  $0 \rightarrow P_n$ ,  $n = 8, 10, 12$  bands of methane for  $T = 295 \text{ K}$  and  $\text{FWHM} = 0.04 \text{ cm}^{-1}$

$n$	$\nu \text{ cm}^{-1}$	$ \langle \mu \rangle  \text{ D}$	$\sigma \text{ cm}^2/\text{mol}$
8	11 300	$2.3 \cdot 10^{-4}$	$3.7 \cdot 10^{-22}$
10	13 760	$6.1 \cdot 10^{-5}$	$3.2 \cdot 10^{-23}$
12	16 135	$1.8 \cdot 10^{-5}$	$3.5 \cdot 10^{-24}$

At the resolution of  $0.04 \text{ cm}^{-1}$ , we may assume that the fine structure of the  $J$ -multiplet caused by the tensorial centrifugal distortion remains unresolved and that consequently,  $F(T, J)$  includes the sum over the components of a single multiplet. For our purposes, we may also further simplify  $F(T, J)$  by using the total degeneracy of the multiplet in place of exact rotational and nuclear spin factors, so that

$$F(T, J) \approx (2J + 1)^2 \exp(-J(J + 1) T_r/T) Q(T)^{-1},$$

where  $T_r = hcB/k \approx 7.54 \text{ K}$  and the partition function  $Q(T)$  can be approximated by Eq.(3) of Ref.[51]. For  $T = 295 \text{ K}$ , the  $J = 6$  multiplet is most populated and we have  $F(295, 6) \approx 0.1$ . Assuming a Lorentzian form-factor with  $\text{FWHM} = 0.04 \text{ cm}^{-1}$  being about the minimal collisional line width observed, and taking its value  $(\pi \text{FWHM}/2)^{-1}$  at the center frequency of the spectral line, we arrive at the values for  $\sigma$  in Table VI.

Integral absolute band strengths  $S_{\text{band}}$  of the unresolved  $0 \rightarrow P_n$  bands with  $n = 8, 10, 12$  where estimated experimentally in Refs. [20, 22, 52, 53]. Lucchesini and Gozzini [21] determined cross-sections  $\sigma_{\text{line}}$  for individual rotational lines in the weak  $840 \text{ nm}$  band, a satellite of the main  $0 \rightarrow P_8$  transition at  $889 \text{ nm}$ . Comparing their data to the respective  $S_{\text{band}}$  value and assuming similar  $\sigma_{\text{line}}/S_{\text{band}}$  ratio for  $n = 10, 12$ , gives  $\sigma_{\text{line}}$  values of the same order as those in Table VI. This suggests the utility of Eq. (6) for crude estimates. This also indicates that our experiment (Sec. II) with the estimated minimal cross-section of  $10^{-26} \text{ cm}^2/\text{molecule}$  had a good margin of sensitivity even in the case of  $0 \rightarrow P_{12}$  and that observing rotational structure of the  $0 \rightarrow P_{14}$  band should be within reach of contemporary techniques.

### C. Model transition moment for $\text{CH}_4$

One of the most frustrating problems in the traditional Taylor series based spectroscopic approach [5, 6] to the analysis of direct transitions  $P_0 \rightarrow P_n$  with large  $n \approx 10$  is the absence of any clues as to the possible values of the parameters of the effective transition moment  $\mu_{\text{eff}}$  induced by the vibrations. In such analysis, both the effective polyad Hamiltonian  $\mathcal{H}$  and dipole moment  $\mu_{\text{eff}}$  are Taylor expanded near the equilibrium, and as the work progresses to states in higher excited polyads, higher degrees in both series get involved and their coefficients



TABLE VII: Terms in the transition dipole moment of degree 3 and 4 for excitations of the stretching RE of symmetry  $C_{3v} \times T$ 

Degree	Term	$g_\mu$	STDS tensor definition [4–6]	Coefficient
$\xi^3$	$\mu_{113}$	$t_1^2 t_3$	$z_1^2 \mu_3^{F_2}$	$12 \eta_1 (1 - \eta_1)^{1/2}$
	$\mu_{133}$	$t_1 t_3^2$	$z_1 [\mu_3^{F_2}, \mu_3^{F_2}]^{F_2}$	$12 \eta_1^{1/2} (1 - \eta_1) \sqrt{2}$
	$\mu_{(33)3}^\Gamma$	$t_3^4$	$[[\mu_3^{F_2}, \mu_3^{F_2}]^\Gamma, \mu_3^{F_2}]^{F_2}$	$4 (1 - \eta_1)^{3/2} \sqrt{3}$
				$8 (1 - \eta_1)^{3/2}$
$\xi^4$	$\mu_{1113}$	$t_1^3 t_3$	$z_1^3 (z_4, z_5, z_6) = z_1^3 \mu_3^{F_2}$	$-16 \eta_1^{3/2} (1 - \eta_1)^{1/2}$
	$\mu_{1133}$	$t_1^2 t_3^2$	$z_1^2 [\mu_3^{F_2}, \mu_3^{F_2}]^{F_2}$	$-24 \eta_1 (1 - \eta_1) \sqrt{2}$
	$\mu_{1(33)3}^\Gamma$	$t_1 t_3^3$	$z_1 [[\mu_3^{F_2}, \mu_3^{F_2}]^\Gamma, \mu_3^{F_2}]^{F_2}$	$-16 \eta_1^{1/2} (1 - \eta_1)^{3/2} \sqrt{3}$
				$-32 \eta_1^{1/2} (1 - \eta_1)^{3/2}$
	$\mu_{(33)(33)}^{\Gamma F_2}$	$t_3^3$	$[[\mu_3^{F_2}, \mu_3^{F_2}]^\Gamma, [\mu_3^{F_2}, \mu_3^{F_2}]^{F_2}]^{F_2}$	$-8 \sqrt{6} (1 - \eta)^2$
			$-8 \sqrt{2} (1 - \eta)^2$	

are determined. However, there is a profound difference between the way in which  $\mathcal{H}$  and  $\mu_{\text{eff}}$  are extrapolated. The lower degree terms of  $\mathcal{H}$  can be determined from the analysis of lower polyads, notably  $P_3$  and  $P_4$ , and can be used subsequently to predict—with varying accuracy—the higher excited states. Not so for  $\mu_{\text{eff}}$ : in this traditional approach, in order to describe  $P_0 \rightarrow P_n$ , we have to inject new terms of specific degrees. For large number  $K$  of the vibrational degrees of freedom involved in the polyads, the number of terms to be injected can be quite significant (Sec. IV C 1).

It is clear that any spectroscopic analysis of  $P_0 \rightarrow P_n$  with large  $n$  would require rough initial values of the parameters in  $\mu_{\text{eff}}$ . At the contemporary level of *ab initio* calculations, there is little hope to obtain anything beyond cubic and maybe quartic terms in  $\mu_{\text{eff}}$ . Therefore, we should use more information on the dynamics of the system to confine our description to a smaller number of quantum states which would require smaller number of phenomenological parameters (Sec. IV C 2). We should also think of rewriting  $\mu_{\text{eff}}$  in such a way that it can be extrapolated similarly to  $\mathcal{H}$ .

### 1. Number of linearly independent terms in $\mu_{\text{eff}}$

Recall that in the case of tetrahedral symmetry,  $\mu_{\text{eff}} = \mu_{\text{eff}}^{F_2}$  transforms like any polar 3-vector according to the irreducible representation  $F_2$ . So within the usual framework,  $P_0 \rightarrow P_n$  is described by terms of type  $F_2$  of degree at least  $n/2$  or higher in creation operators  $a^+$ . For example, the term  $(a_1^+)^3 a_3^+$  describes the  $P_0 \rightarrow 3\nu_1 + \nu_3$  transition suggested in Ref. [16, 17]. Clearly, there are much more such terms of degree 4, let alone those of higher degrees that involve bending modes, and the coefficients in front of them are unknown and cannot be derived from the studies of lower polyads.

All terms in  $\mu_{\text{eff}}^{F_2}$  describing the  $P_0 \rightarrow P_n$  transition without recombinations, i.e., terms consisting purely of  $z$  (or of creation operators  $a^+$ ), are described by the gen-

erating function

$$g_\mu = \frac{(t_2^2 + t_2 + 1)(t_3^2 + t_3 + 1)(t_4^2 + t_4 + 1) \chi}{D_1 D_2 D_3 D_4}$$

of four formal variables  $(t_1, t_2, t_3, t_4)$  representing normal mode coordinates  $z_1, z_{2,3}, z_{4,5,6}$ , and  $z_{7,8,9}$ , respectively. The numerator of  $g_\mu$  with

$$\begin{aligned} \chi = & t_4 + t_3 - t_3 t_4 + (t_3 + t_4 + t_2) t_3 t_4 \\ & + t_3 t_4 (t_4^2 + t_3^2) + t_2 t_3 t_4 (t_3 + t_4) + t_2 t_3^3 + t_2 t_4^3 \\ & + t_3^2 t_4^2 + t_3^2 t_4^3 - t_2 t_3 t_4 (t_3^2 + t_4^2) \\ & + t_2 t_4^4 t_3 + t_2 t_3^4 t_4 + t_2 t_3^2 t_4^3 + t_2 t_3^3 t_4^2 - t_3^3 t_4^3 \\ & + (t_4 + t_3 + t_2) t_3^3 t_4^3 \end{aligned}$$

represents  $F_2$ -type covariants; the denominator terms

$$\begin{aligned} D_1 &= 1 - t_1 \\ D_2 &= (1 - t_2^2)(1 - t_2^3) \\ D_3 &= (1 - t_3^2)(1 - t_3^3)(1 - t_3^4) \\ D_4 &= (1 - t_4^2)(1 - t_4^3)(1 - t_4^4) \end{aligned}$$

describe principal totally symmetric (type  $A_1$ ) invariants. Taylor expanding  $g_\mu$  and collecting terms  $t_1^{k_1} t_2^{k_2} t_3^{k_3} t_4^{k_4}$  with  $2k_1 + k_2 + 2k_3 + k_4 = n$  gives a formal representation of the  $P_0 \rightarrow P_n$  effective dipole moment. Each monomial represents a particular type of linearly independent  $F_2$ -covariants; coefficients in front of the monomials indicate the number of covariants of the particular type.

If  $\mu_{\text{eff}}^{F_2}$  is analytic, then terms of higher relative degree in  $t_1$  and  $t_3$  are of lower total degree, and make, therefore, a more important contribution to  $\mu_{\text{eff}}$  and to the intensity of the  $P_0 \rightarrow P_n$  transition. For even polyads, the most important terms in  $\mu_{\text{eff}}$  contain only stretching variables  $t_1$  and  $t_3$ . Thus we have

Polyad	Stretching part of $\mu_{\text{eff}}$
$P_6$	$t_1^2 t_3 + t_1 t_3^2 + 2t_3^3$
$P_8$	$t_1^3 t_3 + t_1^2 t_3^2 + 2t_1 t_3^3 + 2t_3^4$
$P_{10}$	$t_1^4 t_3 + t_1^3 t_3^2 + 2t_1^2 t_3^3 + 2t_1 t_3^4 + 4t_3^5$
$P_{12}$	$t_1^5 t_3 + t_1^4 t_3^2 + 2t_1^3 t_3^3 + 2t_1^2 t_3^4 + 4t_1 t_3^5 + 4t_3^6$

Further interpretation of these expressions and explicit construction of the purely stretching terms is relatively simple because powers of  $t_1$  represent essentially a trivial factor. It follows that we should construct all  $F_2$ -type covariants of a given degree in  $z_{4,5,6}$ , see next Sec. IV C 2, Table VII, and Ref. [54]. For odd  $n$ , the most important  $P_0 \rightarrow P_n$  terms in  $\mu_{\text{eff}}$  are, necessarily, of degree 1 in one of the bending variables  $t_2$  or  $t_4$ . To find the number of required phenomenological parameters, we should sum up all coefficients in the Taylor expansion. Below we give these numbers for the number of all terms, purely stretching terms, and purely  $\nu_3$  terms (the two latter have degree 1 bending contribution for odd polyads).

Polyad	$P_1$	$P_2$	$P_3$	$P_4$	$P_5$	$P_6$	$P_7$	$P_8$	$P_9$	$P_{10}$	$P_{11}$	$P_{12}$
total	1	3	8	20	43	90	169	313	540	917	1480	2356
$\nu_1, \nu_3$	(1)	1	3	2	7	4	14	6	24	10	38	14
$\nu_3$	(1)	1	2	1	4	2	7	2	10	4	14	4

We can see that the total number of possible parameters grows rapidly beyond reasonable. But even the number of purely stretching parameters is relatively large, given that their values are completely unknown. For example, for the analysis of  $P_0 \rightarrow P_{10}$  within the STDS [4–6] framework, we should “guess” the values of four parameters of purely  $\nu_3$  terms, and if  $\nu_1$  is also important—another 6 parameters. We address this problem in the next section.

## 2. RE induced dipole moment

The number of terms in  $\mu_{\text{eff}}$  becomes so large that we need a model of what goes on. In Sec. III C 4 we selected the  $C_{3v} \times \mathcal{T}$  stretching RE for the analysis. Here we assume that the bright state of the  $P_0 \rightarrow P_n$  transition is localized near this RE. Let  $Z = Z_{C_{3v}}(\eta(n), \phi(n))$  define such RE on  $P_n$  in the form (4). Let  $(\xi, \bar{\xi})$  be coordinates along the axis defined by  $Z$  in the original phase space. Then we can represent  $\mu$  as mainly a power series in  $(\xi, \bar{\xi})$ . At first, we can neglect all other small terms in that series.

To have a simple example, let us assume no bending content ( $\eta_2 = \eta_4 = 0$ ) in  $Z$ , and let us fix the remaining phase  $\phi_1 = \pi$  as in Ref. [27] and denote  $\eta_1 = \eta(n)$ . Let us also distinguish the four different equivalent  $C_{3v} \times \mathcal{T}$  RE by vector-subscripts

$$\alpha = [1, 1, 1], \quad [-1, -1, 1], \quad [1, -1, -1], \quad [-1, 1, -1],$$

one for each of the four axes  $C_3$  in Fig. 2. Then according to Eq. (4) we have

$$Z_\alpha = \sqrt{n} [-\sqrt{\eta}, (0, 0), \sqrt{1-\eta} \frac{\alpha}{\sqrt{3}}, (0, 0, 0)]$$

and therefore

$$\xi_\alpha(z) = -\sqrt{\eta} z_1 + \sqrt{\frac{1-\eta}{3}} \alpha \cdot (z_4, z_5, z_6)^T.$$

Vectors  $\xi_\alpha$  represent distortions caused by four stretching RE of the system. In order to reach polyad  $P_{2s}$ , we should excite either one of them by  $s$  stretching quanta in a row. This means that  $\mu$  should include terms  $\xi_\alpha^s$ . Once this is understood, all we have to do is to construct components of the 3-vector  $\mu^{F_2}$  (with respect to coordinate axes in Fig. 2) by combining the monomials  $\xi_\alpha^s$  appropriately. To this end, we note that  $\xi_\alpha^s$  with  $s = 1, 2, 3, \dots$  are permuted by the operations of  $T_d$  in the same way as  $\xi_\alpha$ . Therefore [70], we can combine four  $\xi_\alpha^s$  in the same way as four  $\xi_\alpha$  in order to obtain the three components of vector

$$\mu^{F_2} = \begin{pmatrix} +1 & -1 & +1 & -1 \\ +1 & -1 & -1 & +1 \\ +1 & +1 & -1 & -1 \end{pmatrix} \begin{pmatrix} \xi_{[1,1,1]}^s \\ \xi_{[-1,-1,1]}^s \\ \xi_{[1,-1,-1]}^s \\ \xi_{[-1,1,-1]}^s \end{pmatrix}.$$

Substituting expressions for  $\xi_\alpha$  and expanding, we express  $\mu^{F_2}$  in terms of normal mode coordinates  $z_k$ . The result may have several terms but it depends on a single mixing parameter  $\eta = \eta_1$ . Specifically, for each degree  $s$  in  $z$ , we can express  $\mu^{F_2}(z, \eta)$  as a linear combination of STDS tensor operators [4–6] constructed from  $z_1^{A_1} = z_1$  and  $\mu_3^{F_2} = (z_4, z_5, z_6)$ . Results for  $s = 3$  and  $s = 4$  are given in Table VII. Thus for  $s = 4$ , the dipole moment  $\mu^{F_2}(z, \eta)$  can be expressed using six tensors, while for  $s = 3$  we use four tensors. Replacing  $z_k$  by quantum creation operators  $a_k^+$ , we arrive at the wanted quantum transition moment operator  $\hat{\mu}^{F_2}$ .

Note that the formal tensor construction of powers  $[\mu_3^{F_2}]^s$  in Table VII with all possible intermediate irreducible representations  $\Gamma$  gives redundancies.  $\Gamma = A_2$  and  $F_1$  are excluded automatically because, obviously, only even powers, i.e., invariant with respect to permutations, can be built. Furthermore, the number of linearly independent terms of degree  $s$  and symmetry type  $F_2$ , which can be constructed from  $\mu_3^{F_2}$  is given by the coefficients in front of the respective powers in the Taylor expansion of the generating function [54]

$$g_3^{F_2}(t_3) = (t_3 + t_3^2 + t_3^3)/D_3 = t_3 + t_3^2 + 2t_3^3 + 2t_3^4 + \dots$$

So there are only two cubic and two quartic terms and in each case, among three possibilities with  $\Gamma = A_1, E, F_2$  one should be excluded, i.e., one coefficient should be set exactly to 0. In Table VII, we have chosen to exclude  $\Gamma = E$ .

Furthermore, our results in Sec. III C 1 suggest that, unlike in a local mode system, the  $\nu_1$  content in the  $C_{3v} \times \mathcal{T}$  RE of  $\text{CH}_4$  remains low (about 1% for  $n = 8$ ). Consequently, terms of nonzero degrees in  $\eta_1^{1/2}$  are strongly discriminated and can be neglected. This contradicts the hypothesis of Boraas et al. [16, 17] which implies high  $\nu_1$  content and which was made largely for the sake of simplifying tentative line assignments.

## V. DISCUSSION AND RESULTS

At the base of all contemporary extremely sophisticated attempts [5, 7, 8] to analyze spectroscopic data on excited rovibrational states of methane (and similar systems) is the Taylor expansion in dynamical variables  $(q, p)$  at the equilibrium. Clearly, this becomes increasingly inadequate as we ascend higher up in energy both in terms of convergence and the sheer number of parameters. We believe that progress will not always be possible through accumulation of computer power and models that stem essentially from 1930's. In this work, we attempted to investigate alternatives and complementary approaches and to foresee the future of this field. The idea is to uncover a small part of the polyad  $P_n$ , which is distinguished dynamically and is visible in the  $P_0 \rightarrow P_n$  experiment, and to confine the analysis accordingly.

### A. Vibrational localization in methane

One of our principal objectives was understanding vibrational localization in higher polyads which would allow selecting a small group of excited vibrational states that we observe. We have not resolved this problem definitely for several reasons: low cutoff in the Taylor series for the vibrational Hamiltonian, restriction to purely stretching modes, and neglect for rotation-vibration interactions. Indeed, our present analysis relied on the purely vibrational quartic Hamiltonian  $\mathcal{H}$ . From Table II, we can see that several terms in  $\mathcal{H}^2$ , notably  $t_{3333}^{A_1}$  and  $t_{1313}$  describing stretching modes, are excessively large and that such  $\mathcal{H}$  can hardly be considered as a well behaving converged series. So information on higher degree terms from spectroscopic sources [7, 8], *ab initio* predictions [14, 55, 56], and Morse potential models should be incorporated. We have seen that bending modes were involved in a number of bifurcations of stretching RE and cannot therefore be disregarded. Finally, methane has relatively large rotational constant  $B$  and strong rotation-vibration interactions which cause, in particular, mixing of vibrational modes. The most important lowest order Coriolis interactions of type  $[q \times p] \cdot j$  may result in bending-stretching mixing, higher order terms may couple stretching modes. All these aspects can be incorporated in our analysis without any significant extensions of the theory and will result in a more reliable description of the RE structure of polyads and in extending this description by an additional parameter, the amplitude of the total angular momentum  $j$ .

### B. Interpretation of the $P_0 \rightarrow P_n$ spectra

Traditionally, the  $P_0 \rightarrow P_8$  transition was assigned to an overtone of the fully symmetric stretch  $\nu_1$  and one quantum of the dipole active  $\nu_3$  mode. The most plausible explanation of the  $P_0 \rightarrow P_n$  spectra that we have

come up with as a result of the present study is quite different. We proposed a concrete vibrational assignment in terms of vibrational relative equilibria and explain it. Out of 9 vibrational degrees of freedom we suggested to focus on a particular one, which is, however, neither a naive normal mode overtone, nor a simple "local mode" (LM) vibration of a particular chemical bond C-H.

We believe that our  $P_0 \rightarrow P_n$  spectra involve a small group (cluster) of bright and dark upper states localized near the  $C_{3v} \times \mathcal{T} n\nu_3$  RE. Because we deal with the same isotropy as in the case of LM's, the number of states and the symmetry properties of the cluster are the same. We have four states split into an  $A_1 + F_2$  doublet, in which the  $A_1$  component is dark (in the absence of rotation) and the  $F_2$  component is active. Unlike the LM states, however, the  $\nu_1$  content is negligible.

Comparing to the  $(n-1)\nu_1 + \nu_3$  assignment we may note a number of strong points in our favor. Most importantly, a transition to an appropriate  $C_{3v}$  localized  $n\nu_3$  state is likely to be by orders of magnitude stronger than  $(n-1)\nu_1 + \nu_3$ . Furthermore, because it involves vibrations about the  $\nu_1$  RE, the  $(n-1)\nu_1 + \nu_3$  state is less likely to be localized and less likely to have such a simplistic normal mode characteristics. Further clarification of this situation can be given after computing stability of the RE in question and frequencies of oscillations about them.

Returning to our proposed assignment, it can be tested in a number of ways. A complete rovibrational polyad computation of the  $0 \rightarrow P_n$  spectrum (using, for example, the STDS program [4-6]) with the dipole moment in Sec. IV C 2 may be attempted and the vibrational states that become involved in the transition may be identified subsequently. Such computation requires considerable resources but is technically possible. In the simplest approximation for even polyad numbers  $n$ , one may attempt to interpret the involved states as part of a purely  $n\nu_3$  stretching polyad localized near the  $C_{3v}$  RE (and thus follow the older work [3, 46]). Such localized states would constitute a cluster of four states composed of states with smallest value of the vibrational angular momentum  $l$ . For even and odd  $n$ , this would involve  $l = 0, 2$  and  $l = 1, 3$ , respectively. Computations in such approach become less heavy. One should note, however, that the rest of the  $n\nu_3$  states has to be disregarded since entire isolated stretching polyads do not exist in methane. Finally, it may be possible to reproduce the rotational structure of such states using an appropriate effective rotational Hamiltonian of a four-well  $C_{3v}$  symmetric top. This should be similar to the local mode formalism of Ref.[23], albeit the wells do not correspond to the four C-H local modes but are formed by the  $\nu_3$  mode alone.

Prior to such attempts, we should follow the outline in Sec. III C and demonstrate more convincingly that the localization of the  $C_{3v} \times \mathcal{T} \nu_3$  type does indeed occur. If that is confirmed, it is quite likely that the individual rovibrational transitions reported in Sec. II can be interpreted satisfactorily on the basis of our vibrational

assignment and treated subsequently within a standard spectroscopic approach.

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- [61] Recall that cubic groups have irreducible representations of dimension 1, 2 and 3, denoted  $A$ ,  $E$ , and  $F$ , respectively.
- [62] The names dyad, pentade, etc reflect the number of normal mode components—not the actual total number of vibrational states. So, taking the degeneracies into account, the respective numbers of states in the dyad and pentade are 5 and 19.
- [63] Nonlinear normal modes were introduced in Refs.[41, 42, 57], a more concrete molecular application was given in Ref. [43]. Within the polyad framework, they were treated later as relative equilibria [3, 27].
- [64] V. Boudon, private communication on the computation for  $0 \rightarrow P_8$  using currently known spectroscopic Hamiltonian of methane.
- [65] For a nonlinear  $s$ -atomic molecule,  $K = 3s - 6$ .
- [66] For an introduction to relative equilibria and definitions, see Appendix 5C of Ref. [58] and Chap. 3.3 of Ref. [59]; for a more specific discussion, see Ref. [60]
- [67] In a more rigorous context, we should be more explicit in describing a  $G$ -invariant subspace. In addition to points with stabilizer  $G$ , it may (and usually does) contain points with higher stabilizers  $G' \supset G$ . Obviously, such subspace corresponds to a union of certain isolated components of several non-generic strata. This also means that  $T_d \times \mathcal{T} \supseteq G' \supset G$  acts nontrivially on it, i.e., the image of  $T_d \times \mathcal{T}$  is 1. For examples of such subspaces, see Secs. III C 1 and III C 2.
- [68] The difference  $\mathcal{N} - n$  is given by Eq. (2) with  $n_1 = \frac{1}{2}$ ,  $n_2 = 1$  and  $n_3 = n_4 = \frac{3}{2}$ .
- [69] In quantum mechanics, we have  $N = n + \frac{1}{2}$  and the closed normal form in Eq. (5a) corresponds to the well known exact solution for the Morse oscillator system.
- [70] This is equivalent to projecting  $\xi_\alpha^s$  on the rows of the irreducible representation  $F_2$ .