

A new methodology for dealing with time-dependent quantities in anharmonic molecules I: theory

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Abstract Morse oscillator coherent states tool has not witnessed much use or applications in quantum dynamics and non-equilibrium statistical mechanics due to the lack of rules of operations and hence the inability to deal with the Morse time evolution operator while still in the coherent states representation. This paper is about developing these needed operation rules of Morse coherent states and applying them to evaluate time correlation functions and thus be able to look at dynamics. This paper further provides two different approaches to dealing with the Morse oscillator propagator while still in coherent states representation, avoiding resorting to eigenstate representation or any other path integral techniques, such as initial value representation approach. Two approaches (one exact and another approximate) are developed to show how to handle anharmonic time evolution operator when acting on Morse coherent states, and calculate time correlation functions analytically. The Morse oscillator partition function is reproduced using the two approaches so as to test the correctness and applicability of the herein methodology. Additionally, the autocorrelation function is derived for a Morse wavepacket pumped on to the excited state, which is represented by a displaced Morse oscillator. A *unitary transformation* is utilized in order to move from the ground-state nuclear Hamiltonian to excited-state Hamiltonian. Evaluating this autocorrelation function using Morse coherent states representation without the alluded-to-unitary transformation in the future may become possible as more progress is made on this novel approach. Absorption spectra are calculated. It is noticed in those

spectra that while the zero-phonon line (ZPL) does not seem to be measurably affected by anharmonicity and only the phonon-side band (PSB) is *shifted and broadened* in case of weak linear electron–phonon coupling [Huang–Rhys factor (S) is less than unity], both the ZPL and PSB are noticeably affected in case $S > 1$. It is further observed that a Voigt profile (a product of Lorentzian and Gaussian in the time domain) predominates the spectrum in case of an appreciable anharmonicity in the molecule. It is inferred that anharmonicity can be critically significant even at low temperature. It is finally concluded that quadratic exponential in the Morse oscillator energy eigenvalue that emerges presents itself as a Gaussian envelope in the autocorrelation function, leading to broadening, whereas the red shift is attributed only to the anharmonicity.

Keywords Anharmonic molecules · Morse potential · Morse coherent states · Anharmonic dipole moment correlation function · Absorption line shape

1 Introduction

Working with the propagator of Morse oscillator and being able to manipulate it is vitally important for probing spectroscopy and dynamics of anharmonic molecules in condensed systems. In contrast to the harmonic oscillator propagator, that of Morse oscillator is much harder and does not lend itself easily to use. Morse oscillator also features an interesting property, which harmonic oscillator does not have, namely divergent dynamics, as has unequivocally been shown by Cao and Toutounji independently [1–3]. Additionally, dynamical calculations that involve employing Morse oscillator eigenfunctions suffer from numerical instabilities and convergence issues.

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(A long-standing problem in Morse oscillator dynamics or statistical mechanics has been the divergence that arises upon evaluating average values and time correlation functions classically [4] or quantum-mechanically [1, 5]. This particular problem has been elucidated by Toutounji in detail [2–4].) Probing dynamics rendered by Morse oscillator is very challenging as divergence and *essential* singularity issues crop up in the classical limit, leading to a gridlock [4].

In light of the above difficulties that emerge upon employing Morse oscillator to represent molecular vibrations, there have been some efforts in developing more practical techniques to surmount those difficulties. Initial value representation (IVR) technique [6, 7] has extensively been utilized to study spectroscopy and dynamics of anharmonic environment. Equivalently, Mukamel and Yan [8, 9] have developed Liouville space generating function technique to do the same thing IVR does. Additionally, different groups have expended efforts on developing anharmonic ladder operators for the purpose of constructing of Morse oscillator coherent states [10–23], but not much on their utility and the corresponding operations of its coherent states in dynamics. Popov and coworkers, and others, have reported important work on Morse oscillator coherent states [11–14]. As strong as IVR technique is, it requires some preparatory numerics, such as calculating trajectories, besides the intermediate simulation steps in case of anharmonic treatment, whereas formulas developed herein circumvent those steps by directly using Morse oscillator coherent states as basis set leading to manageable expressions, whereby only elementary algebra is required. In other words, while all previous works that have anharmonic time evolution of initial conditions would involve path integral techniques or IVR, the work herein presents techniques to evaluate dynamical quantities without resorting to any integral techniques or eigenstate representation.

My paper on harmonic wavelets utilization in spectroscopy [24], and the work of Lin [25] on anharmonic molecules (showing symmetry breakdown of absorption/emission spectra profiles) have prompted me to consider developing a new methodology that allows the use of anharmonic wavelets that might emanate from Morse nuclear forces that develop while evolving along Morse potential. However, in order to do that, one would have to be able to work with Morse oscillator coherent states that lend themselves readily to use as they will be needed at one's disposal, as building blocks, before constructing anharmonic wavelets. As such, the use of these coherent states will be the unprecedented stepping stone to devising anharmonic wavelets in the future. Although different forms of Morse oscillator coherent states are available in the literature [11–23, 26], they fall short of introducing

rules of operations required for time evolving Morse coherent states. Failing to report results in anharmonic coherent states representation makes it very difficult to continue working with these states, hence no utility in their use.

Evaluating averages starting with Morse coherent states representation and ending with eigenstate representation is straightforward; this, however, makes it impossible to carry out inner product of coherent states, thereby losing the point of utilizing Morse coherent states representation in the first place. For example, attempts have been made to evaluate time evolution on a Morse potential using coherent states representation, but managing to stay in this representation has been unsuccessful. As such, there has not been any report of a closed-form expression, or open form for that matter, of how the Morse oscillator time evolution operator acts on its coherent states while still remaining in the same space of coherent states. (As stated earlier, acting with Morse oscillator time evolution operator on its eigenfunctions is numerically problematic, and direct use of Morse propagator is not any easier). The novelty of the approach(s) presented herein lies in offering *maneuvers* to get around the direct use of Morse coherent states for probing time evolution of dynamical quantities along Morse potential while still keeping the same coherent states representation. These maneuvers are vitally important as direct use of Morse coherent states is not feasible without being thrown out back into Fock space (eigenstate representation). This is essential for probing spectroscopy and dynamics in molecules.

In this article, a novel approach is developed for dealing with the above-cited problems and in turn the *anharmonic time evolution operator* for evaluating time correlation functions using Morse coherent states representation, without recourse to IVR, path integrals, or Wigner representation. I also develop an approximate method that does, effectively, the same thing but is faster to evaluate numerically. Absorption line shapes with different linear displacements, and various values of anharmonicity constants are calculated by Fourier-transforming the corresponding derived time autocorrelation functions. To that end, important observations are accordingly made.

The exact Morse oscillator partition function is reproduced using Morse coherent states in order to test the applicability and correctness of the results presented herein. The aforementioned partition function will also be derived using the herein-developed approximate method of manipulating Morse coherent states for the purpose of further ratification. As such, dynamical quantities such as time correlation functions may readily be calculated using the herein-presented formulas without recourse to calculating integrals as other techniques would entail. The effect of the anharmonicity on the zero-phonon line (ZPL) and

the phonon-side band (PSB) will be examined in the last section. This methodology may readily be extended to calculating nonlinear time correlation functions and constructing Morse wavelets in anharmonic molecules, which will be the subjects of paper II and paper III, respectively.

This paper is organized as follows. Section 2 lays out a brief foundation of Klauder–Perelomov Morse coherent states. Couple new approaches are developed in Sect. 3 while evaluating the Morse oscillator canonical partition function, which will in turn be utilized in Sect. 4 to derive the autocorrelation function of Morse oscillator. Discussion and concluding remarks are made in Sect. 5.

2 Brief account of Morse oscillator coherent states

In order to carry out calculations of average related quantities such as optical dipole moment time correlation function and auto-correlation function, appropriate basis set is needed, for which reason Morse coherent states would be suitable for anharmonic molecules. Therefore, I will need to develop some properties of Morse coherent states to help with the evaluation of correlation functions.

The vibrational Morse oscillator Hamiltonian reads

$$H = \frac{P^2}{2\mu} + D_e(e^{-2\alpha x} - 2e^{-\alpha x}) \quad (1)$$

where P and μ are the momentum and position, and D_e and α (often called Morse parameter) are the depth and width of Morse potential well, respectively. This Hamiltonian may be expressed in terms of the lowering operator A and the raising operator A^\dagger as [14]

$$H = \frac{\hbar\omega_e}{2} (A^\dagger A + AA^\dagger) \quad (2)$$

The lowering operator A and the raising operator A^\dagger are given by

$$A = \sqrt{\frac{\hbar\omega_e}{D_e}} \left(\frac{D_e}{\hbar\omega_e} - \frac{y}{2} \frac{d}{dy} - \frac{y}{4} \right), \quad (3)$$

$$A^\dagger = \sqrt{\frac{\hbar\omega_e}{D_e}} \left(\frac{D_e}{\hbar\omega_e} + \frac{y}{2} \frac{d}{dy} - \frac{y}{4} \right), \quad (4)$$

where the Morse coordinate $y = (4D_e/\hbar\omega_e)e^{-\alpha x}$. While the eigenvalues of the harmonic oscillator are $E_n = \hbar\omega_e(n + 1/2)$, with n being the number of the *harmonic* phonons, that of Morse are

$$\begin{aligned} E_m &= \hbar\omega_e \left(m + \frac{1}{2} \right) - \frac{\hbar\omega_e}{4D_e} \left(m + \frac{1}{2} \right)^2 \\ &= \hbar\omega_e \left(m + \frac{1}{2} \right) - \frac{\hbar\omega_e}{N+1} \left(m + \frac{1}{2} \right)^2 \end{aligned} \quad (5)$$

where m is the number of *anharmonic* phonons with $m = 0, 1, \dots, [N/2]$.

Morse coherent states may be written as a linear combination of the Morse oscillator eigenstates $|m\rangle$ as

$$|z\rangle = \sum_{m=0}^{N/2} \frac{z^m}{\sqrt{\rho(m)}} |m\rangle \quad (6)$$

where $\rho(m)$ will be obtained by using the other definition of Klauder–Perelomov coherent states (un-normalized), namely

$$|z\rangle = \exp(zA^\dagger)|0\rangle, \quad (7)$$

where A^\dagger is the anharmonic raising operator and $|0\rangle$ is the vacuum state of Morse oscillator. Expanding the above exponential in Taylor series and carrying out the A^\dagger operation yields [14]

$$\rho(m) = \frac{N^m \Gamma(m+1) \Gamma(N-m+1)}{\Gamma(N+1)} \quad (8)$$

Note $\rho(0) = 1$ and as $N \rightarrow \infty$, $\rho(m)$ becomes $\Gamma(m+1) = m!$

Assuming that Morse potential will have L finite bound states, the inner product of two coherent states is

$$\langle z|w\rangle = \sum_{m=0}^{L=N/2} \frac{(z^*w)^m}{\rho(m)}$$

One would need the closure relationship in order to evaluate time correlation functions. Guided by the procedure done for the harmonic coherent states closure relationship [27], one may start with the projection operator (assuming the molecule escapes the dissociation so as to warrant completeness of the vibrational bound states)

$$\sum_{m=0}^L |m\rangle\langle m| = I \quad (9)$$

which will lead to the following closure relation in terms of Morse coherent states

$$\int d\sigma |z\rangle\langle z| = I, \quad (10)$$

where the integration measure $d\sigma$ has been evaluated by several groups [13, 14, 20], but the form I use herein is written quite differently since I have chosen my coherent states to be *un-normalized*,

$$d\sigma = \frac{(N+1)}{\pi N \left(1 + \frac{|z|^2}{N}\right)^{N+2}} d^2z, \quad (11)$$

where $d^2z = dx dy$, with $z = x + iy$. One may also express z in polar coordinates as $z = re^{i\theta}$. In the following sections,

couple approaches will be developed while evaluating the Morse oscillator canonical partition function and autocorrelation function.

3 A new approach to surmount a challenging problem when using Morse coherent

3.1 States in spectroscopy and dynamics

Interestingly, direct employment of Morse coherent states as a basis set is not helpful in evaluating time-dependent quantities. For example, as stated in Sect. 1, acting with the Morse oscillator time evolution operator on coherent states does not lead to a manageable expression, nor is it efficiently calculable, as it leads to different subspace such as *Fock space*, as well illustrated below in Eq. 12. (Harmonic coherent states, on the other hand, do not have this problem.) To this end, one can act with the Morse oscillator time evolution operator on Morse coherent state $|z\rangle$ as

$$e^{-iHt/\hbar}|z\rangle = \sum_{m=0}^L \frac{z^m}{\sqrt{\rho(m)}} e^{-iE_m t/\hbar} |m\rangle. \quad (12)$$

Evidently, this takes one from coherent states back to *Fock states*; even worse, the exponential in Eq. 12 has positively growing m^2 dependence, which may cause potential problems (i.e., divergence).

3.2 Exact partition function

One may clearly see this by using the Hamiltonian in Eq. 1 on Morse coherent state $|z\rangle$ to evaluate Morse oscillator canonical partition function

$$Q = \sum_{m=0}^L \langle m | e^{-\beta H} | m \rangle = \frac{(N+1)}{\pi N} \int \frac{\langle z | e^{-\beta H} | z \rangle}{\left(1 + \frac{|z|^2}{N}\right)^{N+2}} d^2 z \quad (13)$$

Evaluating the integral yields

$$Q = e^{-\mathcal{G}} \sum_{k=0}^N e^{-ku+vk^2} \quad (14)$$

where

$$\mathcal{G} = \frac{\beta \hbar \omega_0}{2} - \frac{\chi \beta \hbar \omega_0}{4} \quad (14a)$$

$$u = \beta \hbar \omega_0 (1 - \chi) \quad (14b)$$

$$v = \chi \beta \hbar \omega_0, \quad (14c)$$

where χ is the anharmonicity constant and $\beta = 1/kT$, with k being the Boltzmann constant. Equation 14 is identical to Morse oscillator partition function at all temperatures,

which evidently demonstrates the absolute correctness and applicability of Morse coherent states. To get Eq. 14, these two relationships, without which Eq. 14 may not be derived, must be used

$$e^{-\beta H} |z\rangle = \frac{e^{-\mathcal{G}}}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-\eta^2} |z e^{-u-2\eta\sqrt{v}}\rangle d\eta \quad (15)$$

$$\langle w | z \rangle \cong \left[\frac{w^* z + N}{N} \right]^N \quad (16)$$

There is a second term to inner product in Eq. 16 which does not seem to contribute significantly to the inner product of Morse coherent states, for which reason it has been dropped. Carrying out the integral in Eq. 15 (utilizing Eq. 16) is straightforward and can be evaluated exactly and analytically. Note that e^{vk^2} contributes negligibly at low ($\omega_0 \ll T$) and intermediate ($\omega_0 \approx T$) temperatures.

$$Q = e^{-\mathcal{G}} \left[\frac{1 - 2e^u + e^{2u} + v(e^u + 1)}{e^{-u}(e^u - 1)^3} \right] \quad (17)$$

3.3 Highly accurate partition function

In this subsection, I will develop an approximate closed form of Morse oscillator using its coherent states as further testing of its and applicability.

$$Q = \frac{(N+1)}{\pi N} \int \frac{\langle z | e^{-\beta H} | z \rangle}{\left(1 + \frac{|z|^2}{N}\right)^{N+2}} d^2 z \quad (18)$$

$$e^{-\beta H} |z\rangle = e^{-\mathcal{G}} \sum_{m=0}^L \frac{z^m}{\sqrt{\rho(m)}} e^{-mu+vm^2} |m\rangle \quad (19)$$

Taylor series expanding the quadratic exponential term and keeping the first two terms (higher terms contribute negligibly) yields

$$e^{-\beta H} |z\rangle = \left(e^{-\mathcal{G}} + v \frac{d^2}{du^2} \right) |e^{-u} z\rangle \quad (20)$$

Having Eq. 20 in terms of Morse coherent states is very advantageous as it allows the use of Eq. 16 and hence expressing the final result in a closed form. Multiplying both sides of Eq. 20 by z^* and integrating overall space results in

$$\langle z | e^{-\beta H} | z \rangle = \langle z | e^{-\mathcal{G}} | e^{-u} z \rangle + \left\langle z | v \frac{d^2}{du^2} | e^{-u} z \right\rangle \quad (21)$$

It is important to note that

$$\left\langle z | v \frac{d^2}{du^2} | e^{-u} z \right\rangle = v \frac{d^2}{du^2} \langle z | e^{-u} z \rangle. \quad (22)$$

Using Eqs. 16, 18, and 20–22 and expressing z in polar coordinates as $z = re^{i\theta}$ gives the desired partition function in a closed form

$$Q = \frac{e^{-G-Nu}}{e^u - 1} \left[\left(e^{u(N+1)} - 1 \right) + \frac{v(N + e^u)(e^{u(N+1)} + N - e^u(N + 1))}{N^2(e^u - 1)} \right] \quad (23)$$

Having run calculations (not shown) using the parameters of HCl molecule, Eq. 23 has rendered *excellent* results in comparison with the exact partition function provided in Eq. 14. One can safely claim that Eq. 23 is as excellent as Eq. 14. (One may appreciate the tremendous power of using Morse coherent states by comparing the steps that have led to Eq. 3 as opposed to those that led to an equivalent approximate form (but much less accurate) in 5). Further, if one looks at H₂, HCl, CO, and I₂ molecules, their corresponding N^2 would, respectively, be 1,156 (lightest molecule), 2,916, 25,600, and 16,384. As such, the second term in Eq. 23 contributes insignificantly at low ($\omega_0 \ll T$) and intermediate ($\omega_0 \approx T$) temperatures, leading to

$$Q = \frac{e^{-G-Nu}}{e^u - 1} \left(e^{u(N+1)} - 1 \right). \quad (24)$$

Morse oscillator partition function has been evaluated before using different schemes; however, an analytical expression of the Morse oscillator autocorrelation function has never been reported before. Below, an exact expression and a closed-form (approximate) expression are reported using the techniques developed above.

4 Morse oscillator autocorrelation function

Being able to correctly reproduce the Morse oscillator partition function using its coherent states opens the door to other important dynamical quantities such as optical correlation functions. In this section, I will employ Morse coherent states proceeding along the same lines as above to derive an expression for the autocorrelation function. Starting with the anharmonic vacuum state (ground state of Morse oscillator) $|0\rangle$, the molecular wavepacket is pumped to the vibronic excited state where it evolves under the nuclear force of excited displaced Morse potential. The pump-prop process may be represented by Morse autocorrelation function $F(t)$

$$F(t) = \langle 0|0(t)\rangle. \quad (25)$$

The final state is represented by a linearly displaced Morse potential, keeping the same harmonic frequency as

in the ground state. The ground and excited nuclear Hamiltonians are

$$H_g = \frac{\hbar\omega_0}{2} \left[p^2 + \frac{1}{2\chi} \left(1 - e^{-\sqrt{2}\chi q} \right)^2 \right] \quad (26)$$

$$H_e = \frac{\hbar\omega_0}{2} \left[p^2 + \frac{1}{2\chi} \left(1 - e^{-\sqrt{2}\chi(q-\Delta)} \right)^2 \right],$$

$$F(t) = \langle 0|e^{-iH_e t/\hbar}|0\rangle. \quad (27)$$

where Δ is the upper linear dimensionless displacement with respect to the initial state. $e^{-iH_e t/\hbar}|0\rangle$ is very hard to carry out algebraically; therefore, one may get around that by introducing the following *unitary transformation*,

$$e^{-iH_e t/\hbar} = U^\dagger e^{-iH_g t/\hbar} U \quad (28)$$

U is a unitary displacement operator and takes on this form

$$U = \exp \left[\Delta(A^\dagger - A)/\sqrt{2} \right]. \quad (29)$$

Inserting Eq. 28 in Eq. 27 leads to

$$F(t) = \langle 0|U^\dagger e^{-iH_g t/\hbar} U|0\rangle \quad (30)$$

$$= \langle \Delta/\sqrt{2}|e^{-iH_g t/\hbar}|\Delta/\sqrt{2}\rangle. \quad (31)$$

$|\Delta/\sqrt{2}\rangle$ is a Morse coherent state, and therefore, the above relations used to find the partition function will apply. Equation 31 will be evaluated exactly and approximately, leading to compact expressions.

4.1 Exact Morse oscillator time autocorrelation function

Before evaluating Eq. 31, it should be informative to write out how $e^{-iH_g t/\hbar}$ acts on the anharmonic coherent state $|\Delta/\sqrt{2}\rangle$, since this is first time reported herein,

$$F(t) = \frac{e^{-\mathcal{L}}}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-b^2} \langle \Delta/\sqrt{2}|\Delta/\sqrt{2}e^{-ib\omega_0\chi t + i\omega_0 t(1-\chi)}\rangle db, \quad (32)$$

where

$$\mathcal{L} = i\omega_0 t \left(\frac{1}{2} - \frac{\chi}{4} \right). \quad (32a)$$

Evaluating the integral in Eq. 32 yields

$$F(t) = e^{-\mathcal{L}} \left(1 + \frac{\Delta^2}{2N} \right)^{-N} \sum_{\ell=0}^N \binom{N}{\ell} \left(\frac{\Delta^2}{2N} \right)^\ell \times e^{-i\omega_0 t(1-\chi)\ell} e^{-(\omega_0\chi\ell/2)^2} \quad (33)$$

In case of a multi-mode system, $F(t)$ reads

$$F(t) = \prod_j \left\{ \left(1 + \frac{\Delta_j^2}{2N_j} \right)^{-N_j} \sum_{\ell=0}^{N_j} \binom{N_j}{\ell} \left(\frac{\Delta_j^2}{2N_j} \right)^\ell \times e^{-\mathcal{L}_j - i\omega_j t(1-\chi_j)\ell} e^{-(\omega_j \chi_j \ell / 2)^2} \right\} \quad (34)$$

4.2 Highly accurate Morse oscillator time autocorrelation function

It should be further informative to write out how $e^{-iH_g t/\hbar}$ approximately (highly accurate though) acts on the anharmonic coherent state $|\Delta/\sqrt{2}\rangle$,

$$e^{-iH_g t/\hbar} |\Delta/\sqrt{2}\rangle = \left(e^{-\mathcal{R}(t)} + i\omega_0 \chi t \frac{\partial^2}{\partial E^2} \right) |e^{-E(t)} \Delta/\sqrt{2}\rangle, \quad (35)$$

where

$$E(t) = i\omega_0 t(1 - \chi) \quad (35a)$$

$$\mathcal{R}(t) = i\omega_0 t \left(\frac{1}{2} - \frac{\chi}{4} \right). \quad (35b)$$

Using Eq. 35 in Eq. 31 yields

$$F(t) = e^{-\mathcal{R}(t)} \left\{ \langle \Delta/\sqrt{2} | \Delta e^{-E(t)} \Delta/\sqrt{2} \rangle + i\omega_0 \chi t \frac{\partial^2}{\partial E^2} \langle \Delta/\sqrt{2} | e^{-E(t)} \Delta/\sqrt{2} \rangle \right\}. \quad (36)$$

Evaluating the derivative in Eq. 35 leads to the final form of the autocorrelation function

$$F(t) = e^{-\mathcal{R}(t)} \left(\frac{\Delta^2}{2N} + 1 \right)^{-N} \left\{ \left(\frac{\Delta^2 e^{-E(t)}}{N} + 1 \right)^N + i\omega_0 \chi t \left[\frac{(N-1)N^2 \Delta^6 \left(\frac{\Delta^2 e^{-E(t)}}{2N} + 1 \right)^{2N}}{(\Delta^2 + 2N e^{E(t)})^3} \right] \right\} \quad (37)$$

One may recover the well-known $F(t)$ in the harmonic limit by letting $N \rightarrow \infty$, leading to

$$F(t) = \exp \left[-\frac{\Delta^2}{2} (1 - e^{-i\omega_0 t}) - \frac{i\omega_0 t}{2} \right]. \quad (38)$$

Note that the linear displacement Δ in Eq. 37 is related to Huang–Rhys factor extracted through emission spectra through $S = \Delta^2/2$. The following identity has been utilized to recover Eq. 38:

$$\lim_{N \rightarrow \infty} \left(1 + \frac{y}{N} \right)^N = \exp(y). \quad (39)$$

Equation 38 is consistent with the harmonic $F(t)$ reported in [28].

5 Discussion and concluding remarks

Equation 33 reveals valuable spectroscopic information. Fourier analysis tells us that the fundamental frequency ω_0 is red shifted by $\omega_0 \chi \ell$ and broadened through the Gaussian envelope, $e^{-(\omega_0 \chi \ell / 2)^2}$ (analogous to Doppler broadening). This is rather interesting as one can infer from the Fourier transform of Eq. 33 that the vibrational structure (PSB) of the absorption line shape is represented by a Voigt profile (convolution of a Lorentzian and a Gaussian in the frequency domain). This Voigt profile becomes more pronounced in the PSB as the anharmonicity increases, as the forthcoming calculations will show. In other words, introducing anharmonicity into the autocorrelation function creates vibrational structural heterogeneity as opposed to the harmonic phonons.

Figure 1 shows linear absorption spectral line shapes calculated by Fourier-transforming Eqs. 33 (exact anharmonic), 37 (approximate anharmonic), and 38 (harmonic linear electron–phonon coupling ($\chi = 0$)) using $\omega_0 = 30 \text{ cm}^{-1}$, $\Delta = 1$, and $\chi = 0.0125$. Harmonic linear electron–phonon coupling spectra will always be represented by a dashed curve in all figures. Although the three spectra appear indistinguishable, one can barely observe some traces of the dashed curve at fundamental $\omega_0 = 30$ and 60 cm^{-1} (overtone). As the bond length ($\Delta = 2$) increases upon excitation by one unit, the anharmonicity ($\chi = 0.0125$) starts to display slight deviations in the progression members (PSB), but the ZPL profile in both spectra is still indistinguishable as shown in Fig. 2. With the upper linear displacement kept fixed at $\Delta = 2$ (Fig. 2) and increasing the anharmonicity to ($\chi = 0.015$) as shown in Fig. 3, the PSB experiences little more deviation than that in Fig. 2, while the ZPL profiles in the anharmonic and harmonic spectra still coincide perfectly. (This shifting and broadening become significant as χ increases, which will lead to broader Morse potential and very less bound states, as is evidenced in Figs. 4 and 5. This finding only reinforces our finding using MQCD formalism [4]. The anharmonic system in Figs. 4 and 5 represents the vibrational dynamics of an O_2 dimer adsorbed on a Pt surface, where $\chi = 0.0335$ [29].) One can observe, on comparing Figs. 4 and 5, that the magnitude of the bond length change upon excitation can lead to broadening and red shifting although the anharmonicity ($\chi = 0.0335$) is kept the same in both figures. Note that while the ZPL profile was not affected in Fig. 4, it did change in Fig. 5 upon changing Δ . It appears from Fig. 5 that changing Δ (such that it is a strong linear coupling) and a slight change in χ value may lead to appreciable change in the ZPL and PSB structures in the absorption band. This evidently shows that anharmonicity can play an important role in spectroscopy and

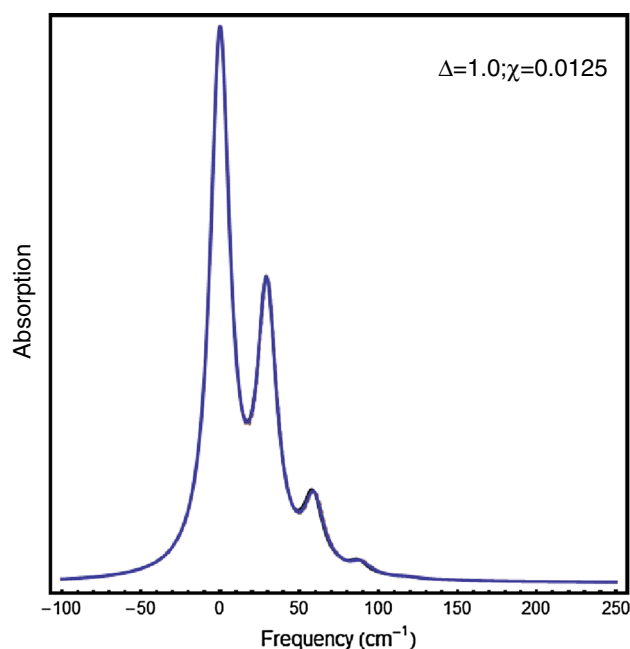


Fig. 1 Three homogenous absorption spectra calculated by Fourier-transforming Eqs. 33, 36, and 37 with the parameters shown in the figure. Harmonic (*dashed brown*) and anharmonic (*solid*) spectra match well

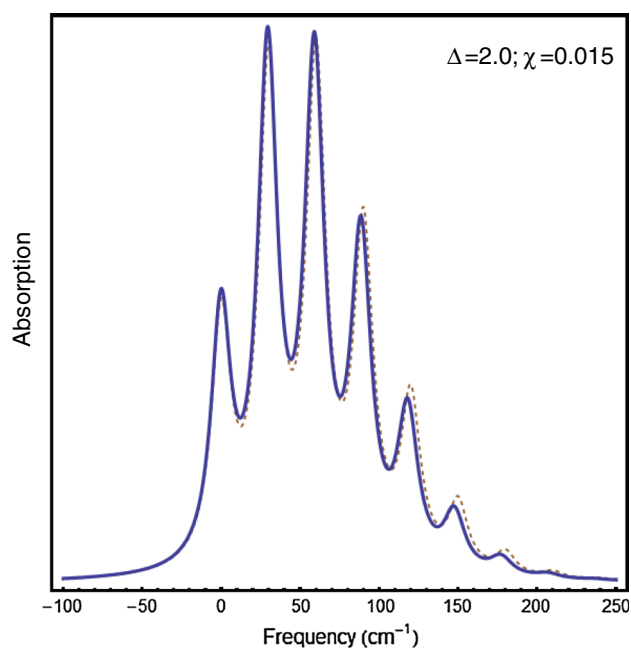


Fig. 3 Harmonic (*dashed brown*) and anharmonic (*solid*) absorption spectra calculated using Eqs. 33 and 37 with the parameters shown in the figure. The anharmonicity constant has increased while the linear displacement ($\Delta = 2$) is kept the same so as to see the deviation caused by the anharmonicity

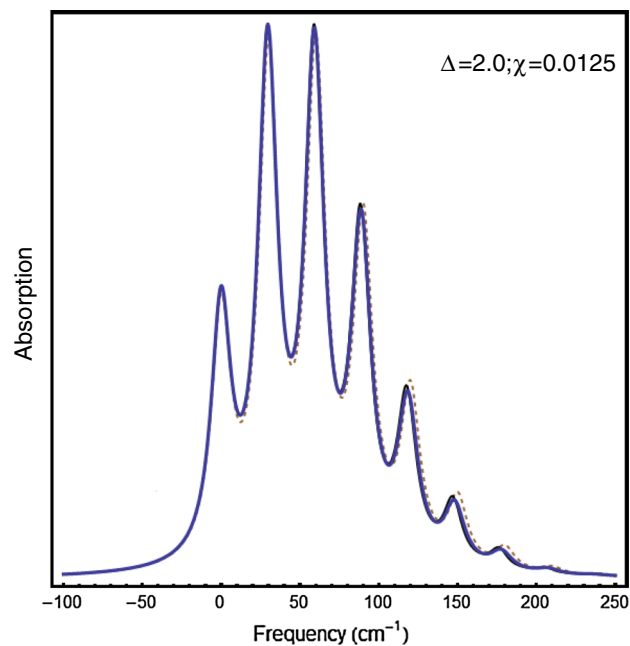


Fig. 2 The same as in Fig. 1 but with larger linear displacement ($\Delta = 2$). One can see that a strong linear electron–phonon coupling ($S > 1$) causes deviation from the anharmonic spectrum for the anharmonicity value in Fig. 1, which shows no deviation for $S < 1$, as comparing Figs. 4 and 5 will confirm this observation

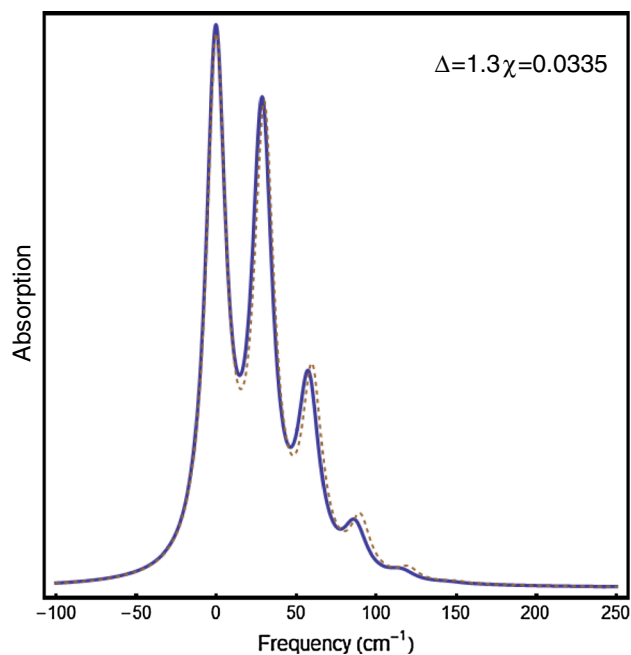


Fig. 4 Harmonic (*dashed brown*) and anharmonic (*solid*) absorption spectra calculated using Eqs. 33 and 37 with the parameters shown in the figure

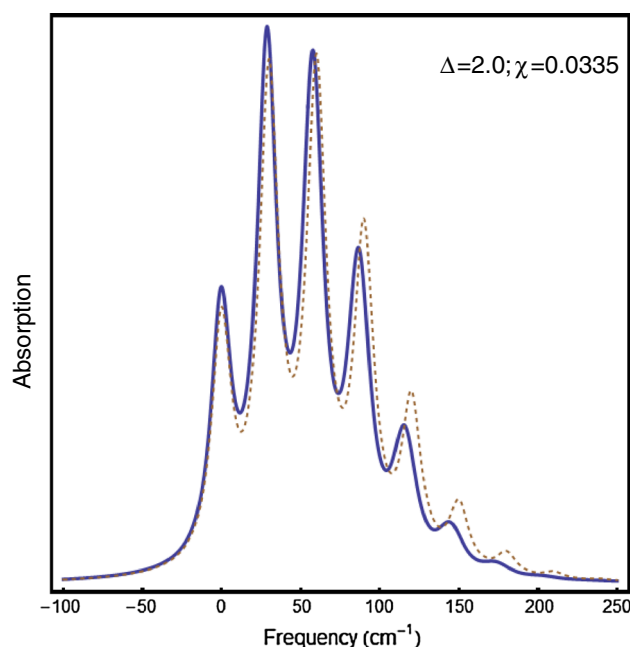


Fig. 5 Harmonic (*dashed brown*) and anharmonic (*solid*) absorption spectra calculated using Eqs. 33 and 37 with the parameters shown in the figure. Figures 4 and 5 serve as to what happens when there is a strong linear electron–phonon coupling ($S > 1$); there is a noticeable disparity between the two spectra upon changing Δ while keeping χ constant

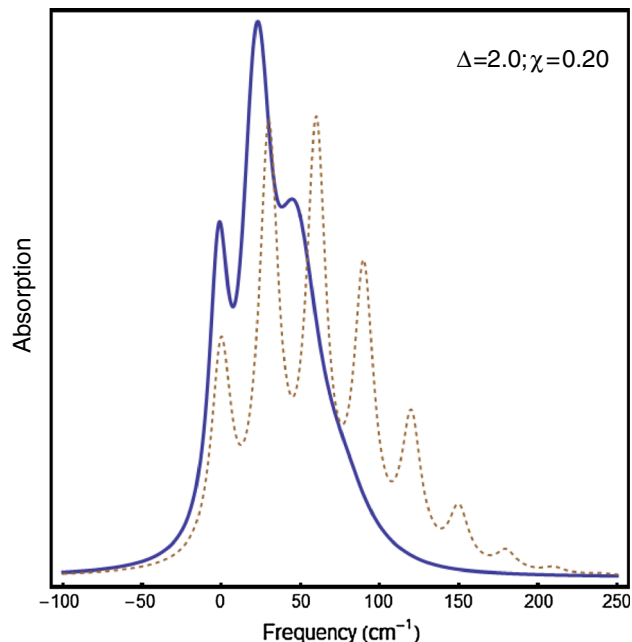


Fig. 6 Harmonic (*dashed brown*) and anharmonic (*solid*) absorption spectra calculated using Eqs. 33 and 37 with the parameters shown in the figure. In the anharmonic spectrum ($\chi = 0.20$), one can observe the dominant effect of the Gaussian profile (Doppler broadening like) whereby a significant deviation is caused between the two spectra at $T = 0$. As such, anharmonicity cannot always be neglected even at low T

dynamics, as is especially shown in Fig. 6, at zero Kelvin. Further, one can evidently see the PSB structural heterogeneity (*vide supra*) in Fig. 6 which is attributed to the dominance of the Voigt profile, $e^{-(\omega_0 t \ell / 2)^2}$. Equations 33 and 37 also reveal that the Franck–Condon factor (FCF) for the anharmonic ZPL is

$$\text{FCF}_{\text{ZPL}} = \left(1 + \frac{\Delta^2}{2N}\right)^{-N}, \quad (39)$$

from which the FCF of the ZPL in case of linear electron–phonon coupling by setting $\chi \rightarrow 0$, yielding $\exp[-S]$.

As pointed out in the Introduction, the motivation for this work is threefold. First, the maneuvers developed in Sects. 3 and 4 will allow calculating anharmonic spectra, for which the dipole moment time correlation function is required, which will further allow an exploration of Lin’s [25] observation of the breakdown of the absorption/emission mirror symmetry without going through the multi-step integrations as was done in [25]. Second, this methodology may readily be extended to calculating *non-linear* time correlation functions and constructing Morse wavelets in anharmonic molecules. This will also allow one to test absorption/emission mirror image [25] deviation in nonlinear signals such as hole-burning and fluorescence line narrowing (FLN) techniques (paper II).

This will lead to paper II. Finally, being able to probe excitation profiles from Morse coherent states will allow building anharmonic wavelets as was done in [24]. Paper III will construct wavelets to represent excitation in anharmonic molecules.

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