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# Efficient Semiclassical Dynamics for Vibronic Spectroscopy beyond Harmonic, Condon, and Zero-Temperature Approximations

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*Abstract:* Understanding light-induced processes in biological and human-made molecular systems is one of the main goals of physical chemistry. It has been known for years that the photoinduced dynamics of atomic nuclei can be studied by looking at the vibrational substructure of electronic absorption and emission spectra. However, theoretical simulation is needed to understand how dynamics translates into the spectral features. Here, we review several recent developments in the computation of vibrationally resolved electronic spectra (sometimes simply called 'vibronic' spectra). We present a theoretical approach for computing such spectra beyond the commonly used zero-temperature, Condon, and harmonic approximations. More specifically, we show how the on-the-fly *ab initio* thawed Gaussian approximation, which partially includes anharmonicity effects, can be combined with the thermo-field dynamics to treat non-zero temperature and with the Herzberg-Teller correction to include non-Condon effects. The combined method, which can treat all three effects, is applied to compute the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ absorption spectra of azulene.

**Keywords**: Absorption spectroscopy · Anharmonicity · Computational chemistry · First-principles calculations · Time correlation function

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## 1. Introduction

Electronic spectroscopy is the most widely used experimental technique for studying excited electronic states of molecules.[1] Electronic spectra offer not only information on the electronic structure but also an insight into the photoexcited nuclear dynamics on the potential energy surfaces of the involved electronic states. However, the abundance of information encoded in the vibrationally resolved electronic spectra presents a challenge for theoretical modeling.

Computational methods for simulating molecular spectra must involve approximations because the exact solution to the underlying quantum-mechanical problem is unfeasible on modern-day computers.[2] Interpretation of simulations becomes particularly hard when the errors due to different approximations are difficult to disentangle. An example that perfectly illustrates this issue is the benchmarking of electronic structure methods for modeling excited electronic states. This is often performed by comparing the vertical excitation energy,[3–5] *i.e.* the energy gap between the ground and excited states computed at a single molecular geometry, with a perceived 'experimental value'. This value is, in most cases, taken as the energy of the absorption maximum. However, the true vertical energy gap is not an experimental observable. A more accurate way of analyzing electronic structure methods

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would be based on computing full electronic spectra and comparing these directly to the experimental result.[6] Unfortunately, as already mentioned above, the simulation of spectra is a challenge of its own and requires approximations to the involved potential energy surfaces and to the photoexcitation process. In this brief overview, we discuss a recently developed framework that allows us to avoid some of these approximations and to improve upon the existing computational approaches for simulating electronic spectra.

## 2. Common Approximations in Vibrationally Resolved Electronic Spectroscopy

In most textbooks, spectroscopy is introduced through the time-independent state-to-state picture. For the vibrationally resolved electronic, or vibronic, spectroscopy, this is known as the Franck-Condon principle, which describes the spectrum as a sum over all possible transitions between the vibrational states of the ground and excited electronic states.[7] This approach is computationally demanding even for smaller molecules, due to the large number of vibronic transitions. Furthermore, since the vibronic transitions often appear in broad bands, computing individual transitions and broadening them to achieve the resolution of the experimental spectrum is a clear waste of computational resources.

An efficient and increasingly popular alternative is the time-dependent approach to spectroscopy, where the absorption cross-section, or spectrum,[8] is expressed as the Fourier transform

$$\sigma(\omega) = \frac{4\pi\omega}{\hbar c}\,\mathrm{Re}\int_0^\infty dt\, e^{i\omega t} C(t) \qquad (1)$$

of the dipole time correlation function

$$C(t) = \mathrm{Tr}[e^{i\hat{H}_1 t/\hbar}\hat{\mu}e^{-i\hat{H}_2 t/\hbar}\hat{\mu}\hat{\rho}], \qquad (2)$$

where $\hat{H}_i$ are the vibrational Hamiltonians in the ground ($i = 1$) and excited ($i = 2$) electronic states, $\hat{\mu}$ is the transition dipole moment, and $\hat{\rho}$ is the temperature-dependent vibrational density operator of the ground electronic state. Eqn. (2) is, despite its apparent simplicity, almost impossible to solve exactly even for relatively small molecules (*e.g.* those consisting of 5–10 atoms). Therefore, to compute and interpret vibronic spectra, various approximations are invoked, including zero-temperature, Condon, and harmonic approximations (see Fig. 1).

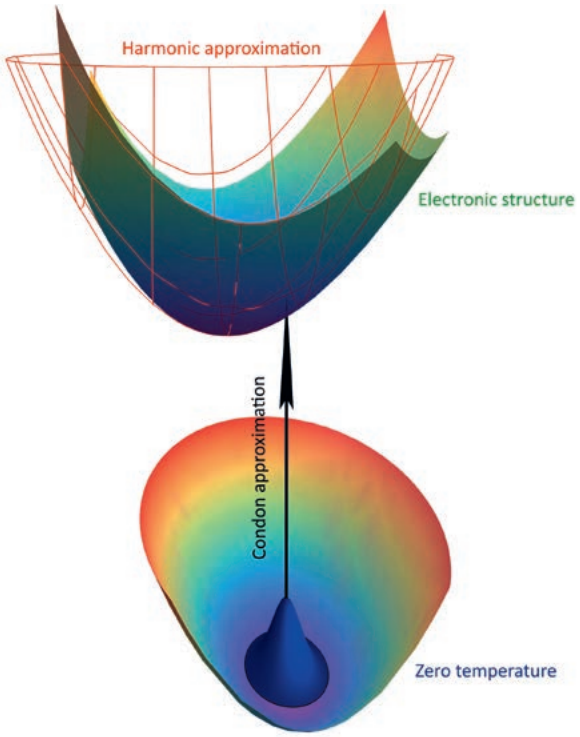


Fig. 1. Schematic view of the photoexcitation process. In the zero-temperature limit, the initial vibrational wavefunction is the ground vibrational wavefunction of the ground electronic state. The Condon approximation assumes that this initial vibrational wavefunction is transferred unchanged to the excited electronic state, where it becomes a non-stationary wavepacket. Its subsequent time evolution is determined by the excited-state potential energy surface, which is often modeled within the harmonic approximation. Errors in the computed electronic spectra arise not only due to the zero-temperature, Condon, and harmonic approximations, but also due to the approximate electronic structure method. However, unless the approximations can be lifted in a systematic way and analyzed independently, their individual contributions to the overall error of the spectrum are difficult to disentangle.

### 2.1 *Beyond Zero-temperature Limit: Thermo-field Dynamics*

At zero temperature, where only the ground vibrational state $|1,g\rangle$ of the ground electronic state is populated, the dipole time correlation function takes the form of an autocorrelation function[9,10]

$$C(t) \approx \langle\phi_0|\phi_t\rangle \qquad (3)$$

of the wavepacket $|\phi_t\rangle = \exp(-i\hat{H}_2' t/\hbar)\hat{\mu}\,|1,g\rangle$ evolved for time $t$ on the excited-state potential energy surface (see Fig. 1), where $\hat{H}_2' = \hat{H}_2 - \hbar\omega_{1,g}$ is the excited-state Hamiltonian corrected by the ground-state zero-point energy $\hbar\omega_{1,g}$. Such a simple and intuitive picture (see Fig. 1) of the photoexcitation process appears to be limited to the zero-temperature picture and is not evident from the finite-temperature expression [Eqn. (2)]. To include non-zero temperature, we could rewrite Eqn. (2) as a Boltzmann-weighted sum

$$C(t) = \sum_n p_n \langle\phi_0^{(n)}|\phi_t^{(n)}\rangle \qquad (4)$$

over the initially populated vibrational states, where $p_n$ are the temperature-dependent Boltzmann factors for the vibrational eigenstates $|1,n\rangle$ of the ground electronic state, $|\phi_t^{(n)}\rangle = \exp(-i\hat{H}_2^{(n)} t/\hbar)\hat{\mu}\,|1,n\rangle$, and $\hat{H}_2^{(n)} = \hat{H}_2 - \hbar\omega_{1,n}$. In other words, finite-temperature effects could be included by averaging autocorrelation functions of different initial wavepackets scaled by the corresponding Boltzmann factors. However, given that typical molecules have thousands or millions of vibrational states with non-negligible thermal population even at room temperature, such a procedure is highly impractical. More efficient approaches that use statistical sampling of initial conditions also exist (see, *e.g.* ref. [11] for an overview). An efficient alternative, based on the so-called thermo-field dynamics,[12–17] has been derived recently.[18] Remarkably, within this new formulation, the dipole time correlation function at arbitrary temperature [Eqn. (2)] can be rewritten as a wavepacket autocorrelation

$$C(t) = \langle\bar{\phi}_0|\bar{\phi}_t\rangle, \qquad (5)$$

but for a wavefunction $\bar{\phi}_0(\bar{q}) = \langle q|\hat{\mu}\hat{\rho}^{1/2}|q'\rangle$ with a doubled number of coordinates, where $\bar{q} = (q, q')$ is the $2D$-dimensional position vector in the doubled configuration space and $D$ is the number of vibrational modes. $\bar{\phi}_t(\bar{q})$ is obtained by propagating $\bar{\phi}_0(\bar{q})$ under the Hamiltonian $\bar{H}_2(\bar{q}) = H_2(q) - H_1(q')$ up to time $t$.[18] As a result, the thermo-field dynamics approach maps the density matrix expression [Eqn. (2)] to the problem of wavepacket dynamics [Eqn.

(5)], which, in analogy with Eqn. (3), can be interpreted as in Fig. 1 and solved with conventional quantum dynamics methods

### 2.2 *Beyond Condon Approximation: Herzberg-Teller Correction*

In general, transition dipole moment is a function of nuclear coordinates, $\hat{\mu} \equiv \mu(\hat{q})$, due to the dependence of the adiabatic electronic states on the molecular geometry. Because this dependence tends to be weak and because the vibrational wavefunctions are highly localized, it is usually valid to assume

$$\mu(q) \approx \mu(q_0), \tag{6}$$

where $q_0$ is some reference point, *e.g.* the ground-state minimum, at which the transition dipole moment is evaluated. This is known as the Condon approximation.[19]

However, when $\mu(q_0)$ is small or, by symmetry, exactly zero, the coordinate-dependence of the transition dipole moment becomes crucial in reproducing the measured spectrum. The first-order, so-called Herzberg-Teller, expansion,[20]

$$\mu(q) \approx \mu(q_0) + \mu'(q_0)^T \cdot (q - q_0) \tag{7}$$

is used in those cases. Ideally, the methods for computing vibrationally resolved electronic spectra should be able to treat non-Condon effects, at least through the first-order Herzberg-Teller correction, since these are regularly encountered in molecules.

### 2.3 *Beyond Global Harmonic Models: Thawed Gaussian Approximation*

The explicit computation of the potential energy surfaces $V_i(q)$ of the ground ($i = 1$) and excited ($i = 2$) electronic states is still unfeasible for all but the smallest molecules. For evaluating vibrationally resolved electronic spectra, one often invokes the global harmonic approximation, where the true potential energy surfaces are replaced by harmonic potentials[21]

$$V_i(q) \approx V_{i,0} + \tfrac{1}{2}(q - q_i)^T \cdot K_i \cdot (q - q_i) \qquad (i = 1, 2), \tag{8}$$

each described by its energy $V_{i,0}$ at the minimum $q_i$ of the harmonic potential and the force constant $K_i$. In the adiabatic harmonic or adiabatic Hessian model,[22,23] the parameters of the harmonic potentials are evaluated at the corresponding equilibrium geometries, $q_{i,\mathrm{eq}}$, *i.e.* $q_i = q_{i,\mathrm{eq}}$, $V_{i,0} = V_i(q_{i,\mathrm{eq}})$, and $K_i = V_i''(q_{i,\mathrm{eq}})$. The model requires only the ground- and excited-state geometry optimizations and the Hessian calculations at these optimized geometries. Such low computational requirements, compared to the exponentially scaling evaluation of the full potential energy surfaces, are partly responsible for the popularity of the harmonic models. Another important reason is the existence of an analytical expression[24–26] for the time correlation function of Eqn. (2), which makes the evaluation of spectra extremely efficient. However, not all molecules can be modeled by harmonic oscillators. Often, the effects of anharmonicity, which are completely neglected in the global harmonic methods, must be included.

Until recently, improvements upon harmonic models were limited to fairly expensive, exact quantum methods.[27] To propagate accurate nuclear wavepackets without precomputing potential energy surfaces, a number of direct dynamics or on-the-fly methods[28–37] were developed, which require only local potential energy information along the trajectories guiding the wavepacket. Most of these employ multiple Gaussian wavepackets, whose propagation can be costly when coupled to the *ab initio* evaluation of the potential energies, gradients, and Hessians.

To offer an efficient and low-cost approach beyond the harmonic approximation, Wehrle *et al.*[38,39] revived the idea of Heller, who proposed a semiclassical method[40] that uses a single Gaussian wavepacket. This method, known as the thawed Gaussian approximation, is based on the fact that a Gaussian wavepacket

$$\psi_t(q) = \exp\left\{\tfrac{i}{\hbar}[(q - q_t)^T \cdot A_t \cdot (q - q_t) + p_t^T \cdot (q - q_t) + \gamma_t]\right\}, \tag{9}$$

described by the $D$-dimensional position ($q_t$) and momentum ($p_t$) vectors, a complex symmetric $D \times D$ matrix $A_t$, and a complex scalar $\gamma_t$, is an exact solution of the time-dependent Schrödinger equation for up to quadratic potentials. To propagate the Gaussian wavepacket (9) in general potentials, the method employs the local harmonic approximation

$$V_{\mathrm{LHA}}(q) = V(q_t) + V'(q_t)^T \cdot (q - q_t) + \tfrac{1}{2}(q - q_t)^T \cdot V''(q_t) \cdot (q - q_t) \tag{10}$$

of the true potential energy $V(q)$ about $q_t$. As a result, the phase-space center ($q_t$, $p_t$) follows a classical trajectory feeling the true, anharmonic potential $V(q)$, while the width of the wavepacket, which is related to the matrix $A_t$, is determined by the Hessians $V''(q_t)$ of the potential along this trajectory. Therefore, the wavepacket is allowed to move according to the fully anharmonic potential, which is not the case in the global harmonic models [Eqn. (8)]. Of course, this semiclassical method is only approximate, since the true wavepacket deforms from its initial Gaussian shape after evolving for long enough in an anharmonic potential. Nevertheless, it is accurate at short times and for moderately anharmonic potentials,[41] which makes it suitable for molecular spectroscopy[38,39,42–44] and ultrafast photoinduced processes.[45] In addition, the method is exact for harmonic potentials because the second-order Taylor expansion of Eqn. (10) becomes exact in this case.

## 3. On-the-fly *ab initio* Extended Thawed Gaussian Approximation for Finite-temperature Spectra

We have now set a framework for improving upon zero-temperature, Condon, and harmonic approximations in a systematic fashion. First, the thawed Gaussian approximation offers a way to propagate the initial Gaussian wavepacket without resorting to the global harmonic model for the excited-state potential energy surface. Second, to account for the Herzberg-Teller correction [Eqn. (7)], the initial state can be generalized to a Gaussian function multiplied by a linear polynomial. Within the so-called extended thawed Gaussian approximation,[46,47] the dynamics of the Gaussian parameters $q_t$, $p_t$, $A_t$, $\gamma_t$ is not affected by the pre-exponential polynomial, meaning that the potential energy data along the excited-state trajectory can be reused for computing either Condon or Herzberg-Teller spectra. Third, to include finite-temperature effects, this extended thawed Gaussian approximation was recently combined with the above-mentioned thermo-field dynamics (section 2.1).[18] The surprising and remarkable result, shown in ref. [18], is that no further potential energy evaluations are needed compared to the zero-temperature case. Therefore, the spectra calculations can be repeated at any temperature, without recomputing the excited-state trajectory or any of the potential energy data.

To compute spectra of arbitrary molecules, for which the potential energy surfaces are not known, we use the on-the-fly *ab initio* approach, where the potential energies, gradients, and Hessians are evaluated only when needed, using the available electronic structure codes. The computational cost of the on-the-fly *ab initio* thawed Gaussian approximation is comparable to the

conventional *ab initio* molecular dynamics. On top of a classical trajectory in the excited electronic state, one must also compute the excited-state Hessians at each step. To reduce the number of Hessian calculations, we recently considered and critically assessed the single-Hessian approximation,[48] where instead of computing multiple Hessians along the trajectory, one Hessian is computed at a reference geometry and used throughout the dynamics. For the range of systems studied in ref. [48], this single-Hessian version was of similar accuracy as the original thawed Gaussian approximation and always more accurate than the global harmonic models.

## 4. Example: Absorption Spectra of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ Electronic Transitions of Azulene

To demonstrate anharmonicity, finite-temperature, and non-Condon effects on vibrationally resolved electronic spectra, we simulate absorption spectra of the first two electronic transitions of azulene. This molecule is famous for violating Kasha's rule,[49] which states that the emission always occurs from the lowest excited electronic state. In contrast to this empirical rule, the emission of azulene occurs from the second excited state $S_2$.[50] The photochemistry of azulene has, therefore, been the subject of many experimental and theoretical studies.[51–55] Yet, until recently,[55,56] there has been no attempt to simulate the $S_2 \leftarrow S_0$ absorption spectrum and surprisingly little was known about it. The recently developed methods based on the thawed Gaussian approximation allowed us to revisit[56] this system from a new perspective.

The lowest-energy electronic band (see Fig. 2) extends from the red to the green part of the visible spectrum and is responsible for the characteristic blue color of azulene. Such a broad band is a direct indication of highly rich excited-state dynamics, where the initial wavepacket is strongly displaced from the excited-state minimum and forms a superposition of many vibrational wavefunctions of the excited electronic state. In such cases, anharmonicity effects tend to play a role. Fig. 2 (top) shows that the harmonic spectrum is fairly accurate at lower frequencies but overestimates the intensity of the high-frequency tail. The on-the-fly thawed Gaussian spectrum is closer to the experiment due to the partial treatment of the anharmonicity effects. The Herzberg-Teller effect is weak, implying that the $S_1 \leftarrow S_0$ transition could be treated accurately within the Condon approximation (see Fig. 2, middle). The finite-temperature effects (Fig. 2, bottom) lead to the broadening of the vibronic bands, affecting also the intensities of certain peaks, *e.g.* those at 14 300 and 15 800 $cm^{-1}$. As a consequence, the finite-temperature version of the thawed Gaussian approximation improves the agreement with experiment.

Remarkably, the three considered effects contribute very differently to the $S_2 \leftarrow S_0$ absorption spectrum of azulene. First, the anharmonicity effects are negligible, as demonstrated by the excellent agreement between the harmonic and thawed Gaussian spectra (see Fig. 3, top). In contrast, the Herzberg-Teller effect (Fig. 3, middle) is now crucial and is responsible for the majority of the observed absorption. Finally, the non-zero temperature (Fig. 3, bottom) affects not only the width of the spectral bands but also the peak positions. For example, the maximum at about 30 600 $cm^{-1}$ appears shifted by ≈100 $cm^{-1}$ if the zero-temperature approximation (red, dashed line in Fig. 3, bottom) is assumed.

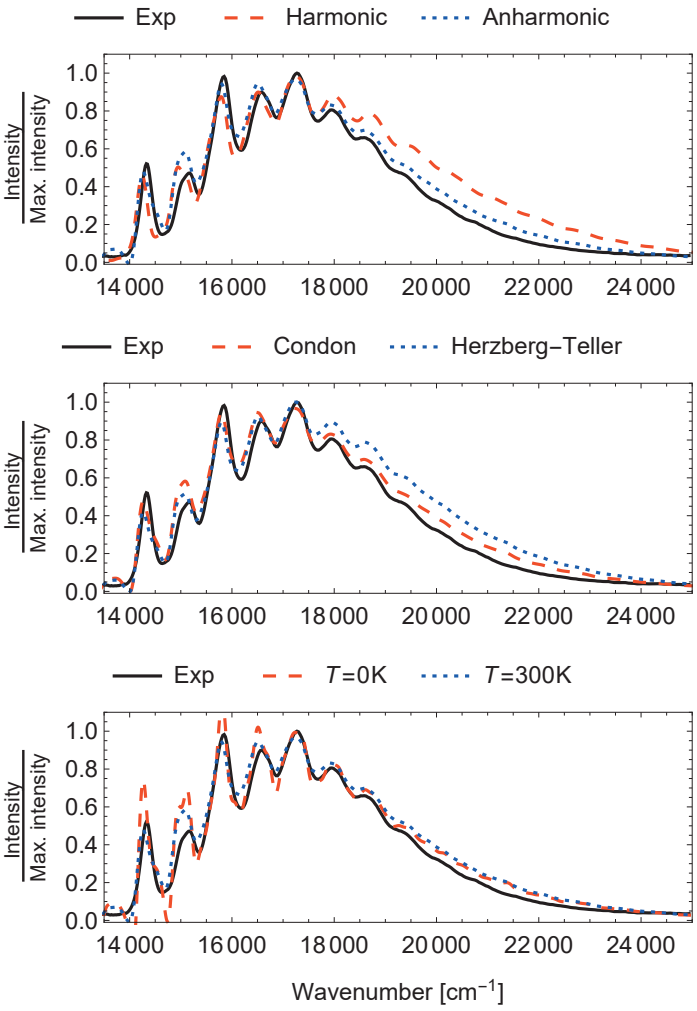


Fig. 2. Computed $S_1 \leftarrow S_0$ absorption spectra of azulene compared with the experimental spectrum[56] (black, solid) recorded in cyclohexane at room temperature. Top: Spectra calculated with the harmonic method (red, dashed) and with the on-the-fly *ab initio* single-Hessian extended thawed Gaussian approximation ('Anharmonic', blue, dotted) at 300 K. Middle: Spectra calculated using the on-the-fly *ab initio* single-Hessian extended thawed Gaussian method within the Condon (red, dashed) and Herzberg-Teller approximations (blue, dotted) at 300 K. Bottom: Spectra calculated with the on-the-fly *ab initio* single-Hessian extended thawed Gaussian approximation at zero temperature (red, dashed) and at 300 K. Second-order Møller-Plesset (MP2) perturbation theory was used to model the electronic structure of the ground electronic state; second-order algebraic diagrammatic construction [ADC(2)] scheme was used for the excited electronic state. Further computational details can be found in ref. [56].

## 5. Conclusions and Outlook

In conclusion, we have presented a set of methods for treating finite-temperature, non-Condon, and anharmonicity effects on vibrationally resolved electronic spectra. The thermo-field dynamics formalism, which is, in our case, the key to computing spectra at non-zero temperature, is formally exact. In contrast, the approach we developed does not treat fully the non-Condon and anharmonicity effects. The Herzberg-Teller approximation is only a first-order correction to the Condon approximation. Higher-order terms in the expansion of the transition dipole moment might play a role in some molecules.[57] This would require a method that can propagate more general initial states. Hagedorn wavepackets,[41,58] which are of the "Gaussian times a general polynomial" form, are a promising solution to this problem. Similarly, the anharmonicity is only partially included in the thawed Gaussian approximation. For strongly anharmonic potential energy surfaces or for high-resolution spectroscopy, where the wavepacket must be propagated for longer times, this approximation might fail. Single-trajectory Hagedorn wavepackets or variational Gaussian wavepacket dynamics[41,59] are two promising methods, which, given additional potential energy data, such as the third or fourth derivatives of the potential energy, could yield more accurate spectra. Importantly, following the work presented here, these wavepacket propagation methods can easily include non-Condon and finite-temperature

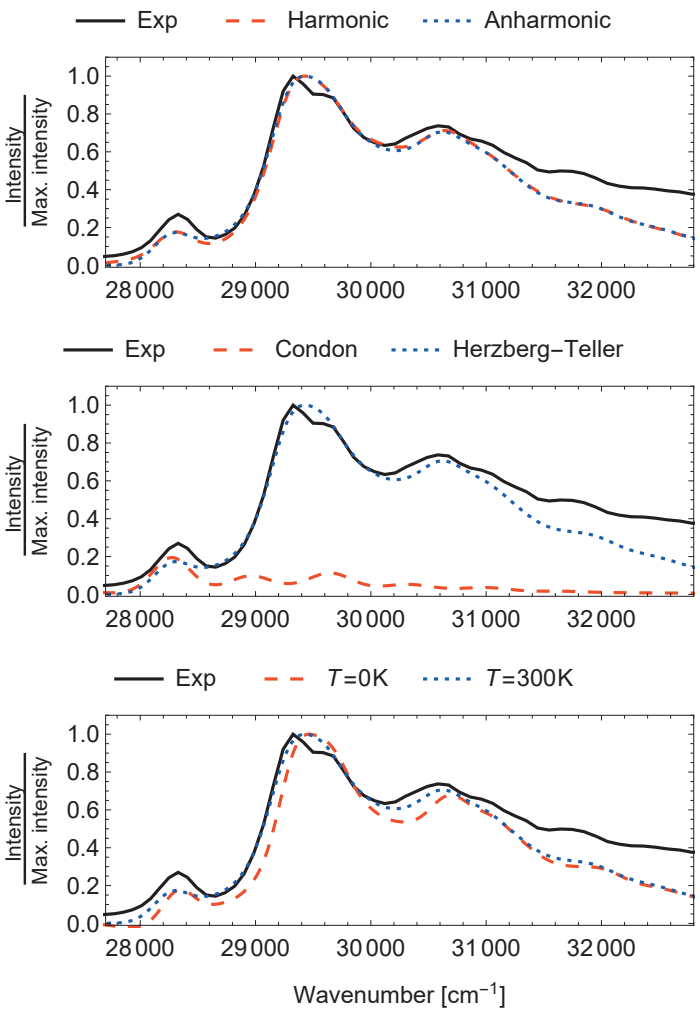


Fig. 3. Same as Fig. 2 but for the $S_2 \leftarrow S_0$ absorption spectrum of azulene.

effects on spectra. Therefore, they could be used to systematically improve upon the existing approaches based on the harmonic and thawed Gaussian approximations.

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