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Simulation of vibronic spectra of flexible systems: hybrid DVR-harmonic approaches

Alberto Baiardi^{*,†}, Julien Bloino^{*,‡,†}, and Vincenzo Barone[†]

[†]Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

[‡]Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, Via G. Moruzzi 1, I-56124 Pisa, Italy

Abstract

Our general framework for the simulation of vibrational signatures in electronic spectra has been extended to treat one large-amplitude motion (LAM) at the anharmonic level, coupled to the other small amplitude motions (SAM) treated as harmonic. The coupling between LAM and SAM is minimized thanks to the use of delocalized internal coordinates, which are built automatically from the molecular topology. General LAMs can be employed, ranging from intrinsic reaction coordinates to rigid or flexible paths based on the distinguished coordinate approach. The anharmonic model is based on a fully-numerical method based on the discrete variable representation (DVR) theory, supporting different types of boundary conditions. The inclusion of this model in a general-purpose electronic structure code makes available to the user a large panel of quantum chemistry models, for both isolated and condensed phases. The flexibility and reliability of the new framework are illustrated by some case studies, covering various types of LAMs, ranging from a small test case, the photoelectron spectrum of ammonia, to larger systems, such as phenylanthracene and cyclobutanone.

1 Introduction

In the last few years, the analysis of vibrational signatures in the electronic spectra of medium- to large-size molecular systems is being increasingly aided by quantum mechanical computations thanks to the development of effective and reliable electronic structure approaches (especially based on the density functional theory (DFT)^{1,2} and its time-dependent (TD) extension^{3,4}), together with improved harmonic vibronic models.^{5–8} Cartesian coordinates, that are currently employed in most cases as a reference set in the evaluation of vibronic effects, are effective and perfectly adequate for semi-rigid systems, with similar structures in the electronic states of interest.^{9,10} Conversely, they are usually inadequate for flexible systems, due to the presence of strong anharmonic effects.^{11,12} This problem is worsened by the fact that couplings between modes are also usually large in cartesian coordinates, so that multidimensional anharmonic treatment are necessary.^{13–15} At variance, curvilinear internal coordinates often reduce those couplings, providing a better description of flexible systems. On those grounds, we have recently introduced general and

* alberto.baiardi@sns.it; julien.bloino@pi.iccom.cnr.it.

effective harmonic vibronic models based on internal coordinates,^{16,17} supporting any kind of molecular topology. Despite notable improvements, harmonic models in internal coordinates remain insufficient if progressions involving large amplitude motions (LAM) are predominant. In most cases, including medium-sized systems, anharmonic effects are important for a single mode, which can be decoupled from the others by employing internal coordinates. For this reason, it is possible to develop hybrid schemes, where a single coordinate is treated variationally, while the other modes are described as harmonic oscillators. The main advantage of such hybrid scheme is the possibility of applying it also to medium-sized systems, unlike full variational approaches, which can be applied only to small (5-6 atoms) molecules.^{13,14} Nevertheless, one-dimensional anharmonic models that are currently used for relatively larger systems lack generality. Indeed, they are usually tailored for specific kinds of large-amplitude motions (such as torsions),^{18–21} or they use semi-empirical Hamiltonians, where some of the parameters are fitted to experimental data.^{22,23} A further issue is that the coupling with the harmonic degrees of freedom is ignored in most cases.

To the best of our knowledge, the model presented in this work is significantly more general than those already available in the literature. First of all, a LAM is parametrized through the so-called intrinsic reaction coordinate (IRC),^{24–26} therefore supporting LAMs defined in terms of arbitrary combinations of internal coordinates. Furthermore, the couplings between the LAM and the other degrees of freedom are included within an adiabatic picture, using the same idea as the well-known reaction path Hamiltonian (RPH).^{27–30} However, studies of the RPH model in conditions similar to the present work have been scarce. First of all, it has been mostly applied to vibrational properties of a single electronic state, and rarely several of them at the same time. The first application of RPH to the calculation of vibronic properties has been proposed, up to our knowledge, for CF₃³¹ and it has been applied to larger systems more recently,³² where however the LAM is treated classically. Next, even if its formulation in terms of a general set of curvilinear, internal coordinates is already known from the work of Truhlar and co-workers,^{29,33,34} most actual applications have been limited to Cartesian coordinates.^{35,36} Regarding the other modes, treated within the harmonic approximation, the machinery developed in the past to compute vibronic spectra at the harmonic level^{9,37,38} can still be applied to its full extent.

The paper is organized as follows. The next section presents the theoretical foundations of the anharmonic model introduced above. After a brief description of the key features of our implementation of harmonic vibronic models in internal coordinates, the anharmonic model used to compute vibrational and vibronic properties for a LAM is presented. Then, the integration of this scheme within both adiabatic and vertical models is discussed in detail. The computational details also contain information on the implementation, and some of its key features are illustrated and discussed through three test-cases: ammonia, phenylanthracene and cyclobutanone.

2 Theory

2.1 Harmonic models for vibronic spectroscopy

As a preliminary step to the description of the anharmonic model presented in this work, let us briefly outline our theoretical framework developed for the simulation of vibrationally-resolved electronic spectra.^{9,37,38} The approach is based on the harmonic approximation for the potential energy surfaces (PESs) of each electronic state involved in the transition, and supports both vertical and adiabatic models.^{9–11} Mode-mixing effects are included through the so-called Duschinsky transformation,³⁹ which is an affine transformation between the normal modes of the initial ($\bar{\mathbf{Q}}$) and final ($\bar{\bar{\mathbf{Q}}}$) states and can be expressed as follows:

$$\bar{\bar{\mathbf{Q}}} = \mathbf{J}\bar{\mathbf{Q}} + \mathbf{K} \quad (1)$$

where $\mathbf{J}$ and $\mathbf{K}$ are the Duschinsky matrix and the shift vector, respectively, and their definition changes with the vibronic model. In the more accurate Adiabatic Hessian (AH) or Vertical Hessian (VH) models, the full transformation is used, and the calculation of the excited-states Hessian matrix is required for computing $\mathbf{J}$. Simplified models with a lower computational cost can be derived by assuming that the harmonic PESs are equal (in practice $\mathbf{J} = \mathbf{I}$). Those models are usually referred to as Adiabatic Shift (AS) and Vertical Gradient (VG), also known as the linear coupling model (LCM).⁴⁰

Within this framework, the following general sum-over-states formula, supporting both one-photon absorption (OPA) and one-photon emission (OPE) spectroscopies, can be derived:

$$I = \alpha\omega\beta \sum_m \sum_n \rho_\gamma \langle \chi_n | \boldsymbol{\mu}^e | \chi_m \rangle \langle \chi_m | \boldsymbol{\mu}^e | \chi_n \rangle \delta \left(\frac{E_n - E_m}{\hbar} - \nu \right) \quad (2)$$

where the values of I and the parameters α , β and γ depend on the specific spectroscopy.⁹ The vibrational wavefunctions of the lower and upper electronic states are labeled as $|\chi_m\rangle$ and $|\chi_n\rangle$ respectively, and $\boldsymbol{\mu}^e$ is the electric dipole moment operator. ν is the wavenumber of the incident (OPA) or emitted (OPE) photon. The dependence of $\boldsymbol{\mu}^e$ on the nuclear coordinates is commonly approximated using a first-order Taylor expansion in terms of the normal modes $\mathbf{Q}$ of one of the two states:

$$\boldsymbol{\mu}^e(\mathbf{Q}) = \boldsymbol{\mu}^e(\mathbf{Q}_{\text{eq}}) + \sum_{i=1}^N \left(\frac{\partial \boldsymbol{\mu}^e}{\partial Q_i} \right)_{\text{eq}} Q_i \quad (3)$$

where the zeroth- and first-order terms are commonly referred to as Franck-Condon (FC) and Herzberg-Teller (HT) approximations, respectively.^{41,42} Using equation 3, the sum-over-states formula given in equation 2 can be expressed in terms of overlap integrals $\langle \chi_m | \chi_n \rangle$, also known as Franck-Condon integrals. At the harmonic level, they can be computed using either analytical^{43,44} or recursive^{45,46} formulae. Some of us have developed a

general framework to compute vibronic spectra using this time-independent (TI) approach,⁹ coupled to a class-based prescreening scheme to select *a priori* the most intense vibronic transitions (see refs.9,37,47,48 for further details). Alternatively, a formally equivalent time-dependent (TD) formulation of vibronic spectroscopy can be derived, which offers several computational advantages with respect to the TI one, especially when temperature effects are needed in the simulation.^{16,38,49}

While the framework described above gives satisfactory results for semi-rigid systems, it suffers from several limitations when dealing with large-amplitude deformations due to the harmonic approximation of the PESs in terms of cartesian coordinates and the Duschinsky transformation itself. As a matter of fact, the latter is built from harmonic normal coordinates so that the reliability of this transformation depends on the accuracy of the description of the molecular vibrations as linear combinations of cartesian-based normal modes. In the presence of highly anharmonic modes, the definition of the Duschinsky transformation becomes inaccurate and a more reliable definition of **J** and **K** requires the use of curvilinear internal coordinates.^{17,50}

The extension of our pre-existing theoretical framework to support a curvilinear set of coordinates is far from being straightforward since all the quantities introduced above must be expressed in terms of this new set of coordinates. The generalization of the Duschinsky transformation can be done following the procedure introduced by Reimers⁵¹ and more recently extended by us to vertical models.¹⁷ This generalization is sufficient to compute spectra at the FC level, since the harmonic frequencies are independent of the coordinate system. Finally, for the specific case of the HT approximation, even the derivatives of the transition dipole moments must be expressed in terms of internal coordinates.¹⁷ A second issue is the definition of a non-redundant set of internal coordinates, which is, at variance with the cartesian case, not univocal for a given molecular structure. A possible set of internal coordinates is made of the so-called primitive internal coordinates (PICs),⁵² which includes all the bonds, valence and dihedral angles, and is uniquely defined by the molecular topology. The number of PICs is usually larger than the number of vibrational degrees of freedom of the molecule, and therefore this basis set is linearly dependent. Several methods have been proposed to define a non-redundant set of internal coordinates as linear combinations of PICs.^{53–57} Among them, our computational tool supports several types of internal coordinates, namely the delocalized internal coordinates (DICs),⁵⁴ Z-matrix coordinates (ZICs),⁵⁵ weighted internal coordinates (WICs)⁵⁷ and natural internal coordinates (NICs).⁵³ Based on the results from previous works,^{16,17} DICs will be used here. They are obtained through a singular value decomposition (SVD) of the PICs-generated Wilson **B** matrix, which is the Jacobian of the transformation between the cartesian (**x**) and internal (**s**) coordinates.⁵⁸

The difference between the definition of **J** in cartesian (**J_x**) and internal (**J_s**) coordinates for systems undergoing large-amplitude deformations lies in the presence of additional, unphysical off-diagonal coupling terms between the large-amplitude mode and the other modes in the former description, which become negligible with DICs. A direct consequence of this mixing is also the presence of a significant number of large components in **K_x**, while only the LAM is strongly shifted in **K_s**. As a result, for simple geometrical deformations, the

LAM can be associated to a single coordinate, which is uncoupled from the other modes in internal coordinates. Therefore, it is possible to improve its description using accurate, high-level monodimensional anharmonic models while keeping the harmonic approximation for the other small-amplitude modes (SAMs). At variance, this can rarely be done employing cartesian coordinates, since the presence of strong couplings requires the use of multidimensional models.¹²

2.2 Selection of the coordinates describing large-amplitude motions

In this section, we will describe an anharmonic variational approach which can be used to compute vibrational properties for a monodimensional LAM. The PES along the LAM is computed explicitly through a scan calculation, and this representation is used to solve numerically the vibrational Schrödinger equation through a variational approach. The scan calculation raises two issues. First of all, the LAM is defined univocally in terms of the internal coordinates $\mathbf{s}$ only at the equilibrium position, where it coincides with one of the harmonic modes (labelled in the following as Q_1). However, the expression of the LAM in terms of internal coordinates is needed also for finite displacements from the equilibrium position to perform the scan. Once this definition is known, the LAM can be expressed as a curve $\mathbf{a}_{\text{LAM}}(z)$ in the internal coordinates space, where the curve has been parametrized through a general parameter z . Depending on z , different representations of the kinetic and potential energy operators can be obtained.

Regarding the first issue, the relation between the LAM and the cartesian coordinates is determined in practice by the computational procedure used to perform the scan. In this work, three different approaches will be employed. The first one is the so-called internal coordinates path hamiltonian (ICPH) model, introduced by Handy and co-workers to describe tunneling processes in malonaldehyde,⁵⁹ and more recently applied to vibronic spectroscopies.³² In the ICPH model, the geometries are obtained by fixing Q_1 at different values and optimizing all other degrees of freedom. It is important to note that, to the best of our knowledge, the ICPH framework has been built for cartesian coordinates, whereas its extension to curvilinear internal coordinates will be used here. An alternative approach is the description of the LAM using the intrinsic reaction coordinate (IRC)^{24–26} combined to the reaction path Hamiltonian (RPH).^{27,60} Within this model, the LAM is defined as the minimum energy path (MEP) connecting a minimum to a transition state. Unlike ICPH, RPH can be used only for PESs with a transition state, such as double-well potentials. On the other hand, it is more general, since it does not require the LAM to be expressed as a fixed linear combination of internal coordinates. Finally, the third model is similar to ICPH but the scan is set rigid instead of relaxed, which means that no geometry optimization is performed during the scan. As will be discussed in the next sections, this model, which will be referred to as non-relaxed ICPH (NR-ICPH), has several limitations, and will be used in the following only for comparison purposes.

Let us now focus on the choice of the parametrization for $\mathbf{a}_{\text{LAM}}(z)$. For simple deformations, the LAM can be expressed as,

$$\mathbf{a}_{\text{LAM}}(z) = \mathbf{s}_0 + z \cdot \Delta \mathbf{s} \quad (4)$$

where $\mathbf{s}_0$ is the vector of internal coordinates computed at a reference geometry and $\Delta \mathbf{s}$ is a fixed linear combinations of PICs. Even if this parametrization has been widely used in the literature^{12,18,61,62} it cannot be coupled to the ICPH and RPH models, in which the expression of the LAM in terms of PICs changes along the because of the structural relaxation. A more general parametrization is obtained by defining the length (l) of the curve $\mathbf{a}_{\text{LAM}}$,⁶³

$$l(z) = \int_0^z dz' \left| \nabla \mathbf{a}_{\text{LAM}}(z') \right|^2 \quad (5)$$

$l(z)$ can be used to parametrize the LAM as $\mathbf{a}_{\text{LAM}}(l)$, and this choice brings several advantages. First, the definition of l holds for any kind of deformation, and therefore is valid for both ICPH and RPH. Next, the expression of the kinetic energy operator is simplified. The form of the kinetic energy operator in a general, curvilinear set of coordinates is,^{64–66}

$$\mathcal{T} = -\frac{\hbar^2}{2} \sum_{kl} g^{1/4}(l) p_k G_{kl}(l) g^{-1/2}(l) p_l g^{1/4}(l) \quad (6)$$

where $\mathbf{p}$ is the momentum operator, g is the determinant of the Wilson $\mathbf{G}$ ⁵⁸ ($g = \det(\mathbf{G})$) and the double sum runs over all internal coordinates. For monodimensional systems, this sum is reduced to,

$$\mathcal{T} = -\frac{\hbar^2}{2} g^{1/4} \frac{d}{dl} g^{1/2} \frac{d}{dl} g^{1/4} \quad (7)$$

where,

$$g = \sum_{k=1}^{3N_{\text{at}}} \left| \frac{dx_k}{dl} \right|^2 = \left| \frac{dx}{dl} \right|^2 \quad (8)$$

As already discussed in the literature,⁶⁵ g is generally a function of l , and therefore equation 7 can be rewritten as a sum of terms containing the first and second derivatives of g . Since they are usually small, these terms can be neglected so that equation 7 can be simplified as,

$$\mathcal{T}(l) = -\frac{\hbar^2}{2} \frac{d}{dl} g \frac{d}{dl} \quad (9)$$

From the definition of l in equation 5, $g = 1$, and therefore the kinetic energy is proportional to the second derivative operator, the same as for mass-weighted cartesian coordinates. It should be remarked that this simplification holds only for monodimensional large-amplitude modes, whereas for multidimensional systems, the Wilson $\mathbf{G}$ matrix must be known explicitly to calculate the kinetic energy operator. 67–69

2.3 The discrete variable representation

The monodimensional vibrational Hamiltonian for the LAM can be expressed in terms of l ,

$$\mathcal{H}^{\text{LAM}}(l) = \mathcal{T}(l) + \mathcal{V}(l) = -\frac{\hbar^2}{2} \frac{d^2}{dl^2} + \mathcal{V}(l) \quad (10)$$

To compute the eigenvalues and eigenfunctions of $\mathcal{H}^{\text{LAM}}(l)$, a variational approach based on the Discrete Variable Representation (DVR) method will be employed. The DVR approach has been introduced by Light and co-workers,⁷⁰ and later rederived by Colbert and Miller⁷¹ as a numerical method to solve the Schrödinger equation. Here, only the most important properties of DVR will be presented, while a more complete discussion can be found elsewhere.^{72,73}

The definition of the DVR theory is strictly related to the variational basis representation (VBR). In VBR, the monodimensional Schrödinger equation is solved by expanding the eigenfunctions as linear combinations of $2n$ polynomials $\varphi_i(l)$ of degree i , which are orthogonal with respect to a weight function $m(l)$ in an interval $[a, b]$. The representation of $\mathcal{H}(l)$ in this basis ($\mathbf{H}(l)$) is obtained computing exactly the integrals $\langle \varphi_i | \mathcal{H} | \varphi_j \rangle$ and the Schrödinger equation is solved by successively diagonalizing $\mathbf{H}(l)$. Even if the integrals of the kinetic operator can be computed analytically for a large number of basis sets,⁷⁴ the exact calculation of integrals involving $\mathcal{V}(l)$ is usually impossible. In DVR, the theory of Gaussian quadrature is used to compute integrals involving $\mathcal{V}(l)$ as follows;

$$\langle \varphi_i | \mathcal{V} | \varphi_j \rangle \approx \sum_{k=1}^n m_i \varphi_i(l_k) \mathcal{V}(l_k) \varphi_j(l_k) \quad (11)$$

where the weight m_i and the grid points $l(l_k)$ (written l_k for simplicity) depend on the quadrature. It has been shown⁷⁰ that this approach is equivalent to transforming the basis $\boldsymbol{\varphi} = (\varphi_1(l), \dots, \varphi_{2n}(l))$ into a new one $\boldsymbol{\chi}^{\text{DVR}} = \boldsymbol{\varphi} \mathbf{C}$ (usually known as the DVR basis set), with the elements of the matrix $\mathbf{C}$ defined as,

$$C_{kj} = \sqrt{\frac{m_k}{m(l_k)}} \varphi_j(l_k) \quad (12)$$

The $\chi_i^{\text{DVR}}(l)$ functions satisfy the localization property $\chi_i^{\text{DVR}}(l_j) = \delta_{ij}$, and the approximated representation of the potential operator $\mathcal{V}$ obtained using equation 11 in the

DVR basis is diagonal ($\langle \chi_i^{\text{DVR}} | \mathcal{T} | \chi_j^{\text{DVR}} \rangle = V(l_i) \delta_{ij}$). On the other hand, the matrix elements of the kinetic energy operator $\mathcal{T}(l)$ between two different DVR basis function can be computed exactly, without invoking equation 11.

Here, three DVR basis sets, which have been proposed in the literature^{74–76} will be used, corresponding to three different choices of the interval $[a, b]$ and of the boundary conditions. The $[0, 2\pi]$ interval is adapted to periodic potentials, thus will be used for any periodic boundary conditions.^{77,78} Another choice is a general $[a, b]$ bounded interval, with the requirement of the wavefunction to be 0 in a and b . The other choice is based on the cardinal sine function (sinc) DVR basis,⁷¹ obtained with open boundary conditions in the $(-\infty, +\infty)$ range. A detailed definition of those basis sets, together with the analytical formulae for the matrix elements of $\mathcal{T}(l)$ is given in the appendix.

The grid $(l_1, \dots, l_n)$ used to compute numerically the Hamiltonian matrix $\mathbf{H}$ is defined by the DVR basis set, but in practice, the grid of l -points in which the energy is computed during a PES scan (the corresponding point will be noted with a tilde) is not known *a priori*. To overcome this problem, a two-steps procedure is adopted. An analytical representation of the PES ($V^{\text{fit}}(l)$) is obtained by fitting the $\tilde{n}$ energies computed at $(\tilde{l}_1, \dots, \tilde{l}_{\tilde{n}})$ using a cubic B-spline.^{79,80} The Hamiltonian matrix to be diagonalized in the DVR calculation is built using $V^{\text{fit}}(l)$ instead of the exact potential. Since $V^{\text{fit}}(l)$ is known analytically, its value at the grid points $(l_1, \dots, l_n)$ is known and can be computed with a negligible computational cost. The number of points needed to obtain a converged representation of the PES from the B-splines is usually significantly lower than the number of grid points needed to reach convergence in the DVR expansion. Therefore, $\tilde{n} \ll n$ in most cases, resulting in a significant gain in computational time, since electronic structure calculations, the bottleneck of the simulation, are performed over a smaller number of points.

This fitting procedure can be easily coupled to the ICPH model, but the integration into the RPH model is less straightforward. Indeed, as shown in the graphical representation of figure 1, the intrinsic reaction path is defined only between the minima and the transition state (green line in figure 1), but $\mathbf{a}_{\text{LAM}}(l)$ needs to be known also beyond this path. Nevertheless, it can be shown that,^{27,33} for infinitesimal displacements from the equilibrium position, the IRC is equivalent to the normal coordinate associated to the LAM and therefore the ICPH model can be used to complement RPH, providing data on $\mathbf{a}_{\text{LAM}}(l)$ beyond the minima (solid, red line in figure 1). For double-well potentials, it is possible to reduce the number of grid points for the ICPH step, by extrapolating the PES using the a double Morse potential, with a functional form,^{81,82}

$$V_{\text{Morse}}(l) = A_1(1 - e^{-b_1(l-l_1)}) + A_2(1 - e^{-b_2(l-l_2)}) \quad (13)$$

where A_1 , b_1 , l_1 , A_2 , b_2 and l_2 are parameters determined through least-squares fitting. The B-spline fitting preliminary to the DVR calculation of the PES along the LAM is then fitted from two components, the analytical expression $V_{\text{Morse}}(l)$ beyond the two end points of the ICPH calculations (dashed, black line in figure 1) and the set of points obtained from

quantum chemical computations built from RPH+ICPH calculations (black and grey crosses in figure 1).

2.4 Hybrid DVR-harmonic models

The previous section described a variational procedure to compute vibrational energies associated to the LAM. However, in order to generate the full vibronic spectrum, the LAM coordinate must be complemented by a set of “ $N_v - 1$ ” coordinates $\tilde{\mathbf{Q}}(l) = (\tilde{Q}_1(l), \dots, \tilde{Q}_{N_v-1}(l))$ describing the remaining “ $N_v - 1$ ” degrees of freedom. It should be noted that, in the most general case, $\tilde{\mathbf{Q}}$ is a function of l . In this subsection, we will describe a strategy to compute the set of coordinates $\tilde{\mathbf{Q}}(l)$ for a single electronic state. In the next subsection, the additional issues to address when dealing with two electronic states, such as in the simulation of vibronic spectra, will be presented.

For a single electronic state, the RPH model provides a consistent definition of $\tilde{\mathbf{Q}}(l)$.^{27,30} Within this framework, the l coordinate is complemented by the “ $N_v - 1$ ” normal modes orthogonal to $\mathbf{a}_{\text{LAM}}(l)$ (referred to as $\mathbf{Q}^p$ in the following). In practice, it is useful to introduce a vector $\mathbf{n}$ tangent to $\mathbf{a}_{\text{LAM}}(l)$ as,

$$\mathbf{n}(l) = \frac{1}{\left\| \frac{d\mathbf{a}_{\text{LAM}}(l)}{dl} \right\|} \frac{d\mathbf{a}_{\text{LAM}}(l)}{dl} \quad (14)$$

which can be used to compute the projector operator in cartesian coordinates on the space parallel to the curve $\mathbf{a}_{\text{LAM}}(l)$ as $\mathbf{P}_x = \mathbf{n}\mathbf{n}^T$. Within the RPH model, $\mathbf{P}_x$ can be rewritten as,

$$\mathbf{P}_x(l) = \frac{\mathbf{g}_x(l)\mathbf{g}_x(l)^T}{\|\mathbf{g}_x(l)\|^2} \quad (15)$$

where $\mathbf{g}_x$ is the energy gradient in cartesian coordinates. When non-orthogonal, internal coordinates are employed, equation 15 does not hold, and the projector $\mathbf{P}_s$ must be computed using the following, more general expression,^{29,33,83,84}

$$\mathbf{P}_s(l) = \frac{\mathbf{g}_s(l)\mathbf{g}_s(l)^T}{\mathbf{g}_s^T(l)\mathbf{G}(l)\mathbf{g}_s(l)} \quad (16)$$

where $\mathbf{g}_s$ is obtained from its cartesian counterpart $\mathbf{g}_x$ from the relation,²⁹

$$\mathbf{g}_s(l) = \left(\mathbf{B}(l)\mathbf{M}^{-1}\mathbf{B}(l)^T \right)^{-1} \mathbf{B}(l)\mathbf{M}^{-1}\mathbf{g}_x(l) \quad (17)$$

where $\mathbf{M}$ is the diagonal matrix of the atomic masses. The discussion will now focus on internal coordinates, hence the expression of the projector given in equation 16 will be used.

The orthogonal modes $\mathbf{Q}^p$ are eigenvectors of $\mathbf{G}\mathbf{H}_s^p$ with the projected Hessian matrix $\mathbf{H}_s^p$ defined as,

$$\mathbf{H}_s^p(l) = [1 - \mathbf{P}_s(l)\mathbf{G}(l)] \mathbf{H}_s(l) [1 - \mathbf{G}(l)\mathbf{P}_s(l)] \quad (18)$$

where $\mathbf{H}_s$ is the full-dimensional Hessian. Those quantities change along the curve $\mathbf{a}_{\text{LAM}}(l)$ and therefore are functions of l . The calculation of the full-dimensional Hessian $\mathbf{H}_s$ from its cartesian counterpart $\mathbf{H}_x$ requires both the Wilson $\mathbf{B}$ matrix and its first derivative $\mathbf{B}'$,^{17,85}

$$\mathbf{H}_s(l) = (\mathbf{B}(l)^T)^+ [\mathbf{H}_x(l) - \mathbf{g}_s(l)^T \mathbf{B}'(l)] \mathbf{B}(l)^+ \quad (19)$$

where $\mathbf{B}^+$ is the pseudo-inverse of $\mathbf{B}$. The projected Hessian $\mathbf{H}_s^p$ has one null eigenvalue associated to the LAM and “ $N_v - 1$ ” non-null eigenvalues $(\omega_i^p(l)^2)$, giving the squared vibrational wavenumber associated to the normal modes orthogonal to the LAM. The eigenvectors associated to the non-null eigenvalues (that are collected as columns of a matrix $\mathbf{L}^p(l)$) define the projected normal modes $\mathbf{Q}^p$ in terms of the internal coordinates as,

$$\mathbf{L}^p(l)\mathbf{Q}^p = \mathbf{s} - \mathbf{s}_{\text{eq}}(l) \quad (20)$$

The vibrational Hamiltonian $\mathcal{H}_{\text{vib}}$ can be expressed in terms of the $(l, \mathbf{Q}^p)$ coordinate set starting from its expression in internal coordinates following the procedure described in refs. 27,30 Without going into details, $\mathcal{H}_{\text{vib}}$ cannot be separated as a sum of two terms, one depending only on l and another only on $\mathbf{Q}^p$ because of the presence of coupling terms, which are proportional to the derivative of the normal modes $\mathbf{L}^p(l)$ with respect to l .⁵⁹ If the LAM is well separated from the other modes, the derivative is nearly null and those coupling terms can be neglected within the so-called adiabatic approximation. In this condition, and assuming that the $\mathbf{Q}^p$ modes can be described within the harmonic approximation, the full vibrational Hamiltonian can be expressed as,

$$\mathcal{H}_{\text{vib}} = \mathcal{T}(l) + \mathcal{V}(l) + \mathcal{T}^{N_v-1}(\mathbf{Q}^p) + \mathcal{V}^{N_v-1}(\mathbf{Q}^p) \quad (21)$$

where $\mathcal{T}(l)$ and $\mathcal{V}(l)$ have been defined in equation 10 and $\mathcal{T}^{N_v-1}(\mathbf{Q}^p)$ is the kinetic energy operator for the “ $N_v - 1$ ” orthogonal modes. The potential $\mathcal{V}(\mathbf{Q}^p)$ can be expanded in a Taylor series about the equilibrium position. Within the harmonic approximation, only one term remain, the second-order one, $\mathcal{V}^{N_v-1}(\mathbf{Q}^p)$, that can be expressed as,

$$\mathcal{V}^{N_v-1}(\mathbf{Q}^p) = \sum_{i=1}^{N_v-1} \frac{1}{2} \omega_i^{p2}(l) Q_i^p(l)^2 \quad (22)$$

Even if the expression of $\mathcal{H}_{\text{vib}}$ obtained using equation 21 does not contain a direct coupling between the LAM coordinate and the orthogonal normal modes, an indirect coupling is present due to the parametrical dependence of ω_i^p and $\mathbf{Q}^p$ on I (as in the Born-Oppenheimer approximation).²⁷ Following the same strategy employed as for the Born-Oppenheimer separation,⁸⁶ the eigenfunctions $\chi(I, \mathbf{Q}^p)$ of $\mathcal{H}_{\text{vib}}$ can be factorized as

$\chi_{i(k)}^{\text{LAM}}(l) \times \chi_k^{\text{Nv}-1}(l, \mathbf{Q}^p)$, where k labels the wavefunction for the harmonic modes, and i the one of the LAM. The two wavefunctions $\chi_{i(k)}^{\text{LAM}}(l)$ and $\chi_k^{\text{Nv}-1}(l, \mathbf{Q}^p)$ satisfy the following two Schrödinger equations:

$$\begin{aligned} \mathcal{H}^{\text{Nv}-1} \chi_k^{\text{Nv}-1}(l, \mathbf{Q}^p) &= [\mathcal{T}^{\text{Nv}-1}(\mathbf{Q}^p) + \mathcal{V}^{\text{Nv}-1}(\mathbf{Q}^p; l)] \chi_k^{\text{Nv}-1}(l, \mathbf{Q}^p) \\ &= E_k^{\text{Nv}-1}(l) \chi_k^{\text{Nv}-1}(l, \mathbf{Q}^p) \end{aligned} \quad (23)$$

$$[\mathcal{T}^{\text{LAM}}(l) + \mathcal{V}^{\text{LAM}}(l) + E_k^{\text{Nv}-1}(l)] \chi_{i(k)}^{\text{LAM}}(l) = E_{i(k)}^{\text{tot}} \chi_{i(k)}^{\text{LAM}}(l) \quad (24)$$

where $\mathcal{H}^{\text{LAM}}$ is defined in equation 10, $\mathcal{H}^{\text{Nv}-1}$ is the sum of $N_v - 1$ harmonic oscillator Hamiltonians and,

$$E_k^{\text{Nv}-1}(l) = \sum_{i=1}^{N_v-1} \omega_i^p(l) \left(n_i + \frac{1}{2} \right) \quad (25)$$

Furthermore, $E_{i(k)}^{\text{tot}}$ is the total vibrational energy. Equations 23 and 24 highlights the indirect coupling between $\mathbf{Q}^p$ and I . In fact, the potential used to compute the LAM wave-functions ($\chi_{i(k)}^{\text{LAM}}(l)$) contains, besides the pure electronic contribution ($\mathcal{V}^{\text{LAM}}(I)$), the energy of the wavefunction for the “ $N_v - 1$ ” harmonic modes ($E_k^{\text{Nv}-1}(l)$). As a consequence, a different set of nuclear wavefunctions for the LAM is obtained for each level of the “ $N_v - 1$ ” harmonic modes. A significant simplification is obtained neglecting the dependence of the harmonic frequencies and normal modes on I since, in this case, the potential $\mathcal{V}^{\text{Nv}-1}$, as well as the vibrational energies $E_k^{\text{Nv}-1}$ do not depend on I . As a consequence, this last term is a constant and the LAM wavefunctions are the same for each vibrational level of the “ $N_v - 1$ ” harmonic coordinates.

2.5 Extension to vibronic models

Extension of this model to support two different electronic states is not straightforward. In principle, the two Schrödinger equations (23 and 24) can be solved independently for the two electronic states, therefore obtaining the wavefunctions of the initial ($\bar{\chi}_n$) and final ($\bar{\chi}_m$) states as $\bar{\chi}_n^{\text{Nv}-1}(l, \bar{\mathbf{Q}}^p) \times \bar{\chi}_{i(n)}^{\text{LAM}}(l)$ and $\bar{\chi}_m^{\text{Nv}-1}(l, \bar{\mathbf{Q}}^p) \times \bar{\chi}_{j(m)}^{\text{LAM}}(l)$, respectively. However, the coordinate systems used in the two electronic states are, in general, different, and this makes the calculation of transition properties between the two states not trivial. For the

harmonic modes, the Duschinsky transformation of equation 1 can be used to relate the two set of modes. Regarding the LAM, the simplest way is to parametrize it using the same curve $\mathbf{a}_{\text{LAM}}(l)$ for both the electronic states. In this way, the PES along the LAM for the two electronic states are known in the same number of points, and this makes the calculation of transition dipole moments easier. To define in practice the curve $\mathbf{a}_{\text{LAM}}(l)$ to use in vibronic simulations, one of the two electronic states must be chosen for geometry optimizations, the same geometries being chosen to compute the PES for the other electronic state. As it will be discussed in the following, if the LAM is uncoupled from the other modes, the effect of changing the reference electronic state to compute $\mathbf{a}_{\text{LAM}}(l)$ is minimal.

The calculation of the orthogonal normal modes of the two states ($\bar{\mathbf{Q}}^p$ and $\bar{\bar{\mathbf{Q}}}^p$ respectively) defines the Duschinsky transformation between the projected modes,

$$\bar{\mathbf{Q}}^p(l) = \mathbf{J}_s^p(l) \bar{\bar{\mathbf{Q}}}^p(l) + \mathbf{K}_s^p(l) \quad (26)$$

where the projected Duschinsky matrix $\mathbf{J}_s^p$ and shift vector $\mathbf{K}_s^p$ change along the LAM coordinate. To derive explicit expressions for $\mathbf{J}_s^p(l)$ and $\mathbf{K}_s^p(l)$, the same strategy already used for the harmonic vibronic models in internal coordinates can be used.^{16,17} For a given value of l , $\bar{\mathbf{Q}}^p$ and $\bar{\bar{\mathbf{Q}}}^p$ can be computed once a reference point has been chosen to perform the Taylor expansion of the PES. The strategy to adopt regarding the expansion depends on the electronic state. For the reference one, used for the definition of the geometries along the relaxed scan (ICPH model) or the reaction path (RPH model), the geometries along $\mathbf{a}_{\text{LAM}}(l)$ can be directly used. Indeed, for those geometries, the gradient components orthogonal to the LAM vanish, and therefore equation 22 can be used to express the vibrational potential and compute the normal modes. For the other electronic state, the choice is less straightforward, and at least two, non-equivalent methods can be followed. A possible choice is to perform the Taylor expansion about the same geometries as for the first state. In this case, equation 22 must be generalized to including also a first-order term, corresponding to the gradient. It is easy to prove that the expression for $\mathbf{J}_s^p(l)$ and $\mathbf{K}_s^p(l)$ are then equivalent to the ones obtained for vertical models, with the projected gradient and Hessian used in place of the full-dimensional ones. More precisely, the definition of the Duschinsky transformation is the following:

$$\mathbf{J}_s^{pT} \bar{\bar{\mathbf{H}}}^p \mathbf{J}_s^p = \bar{\bar{\Omega}}^2 \quad \mathbf{K}_s^p = -\mathbf{J}_s^p \bar{\bar{\Omega}}^{-2} \mathbf{J}_s^{pT} \bar{\bar{\mathbf{L}}}^p \bar{\bar{\mathbf{g}}}_s^p \quad (27)$$

where the projector operator $\bar{\bar{\mathbf{P}}}_s$ is computed by applying equation 16 to the curve obtained with the reference state. The calculation of the Duschinsky matrix is more cumbersome for adiabatic models, since the expansion must be performed about a stationary point also for the second state. This means that, for each value of l , the geometry of the second state must be optimized in the space orthogonal to the gradient of the first electronic state. The

optimized geometries obtained this way ($\bar{\bar{\mathbf{s}}}_{\text{eq}}^p(l)$) can be used to define the Duschinsky transformation,

$$\mathbf{J}_s^p = (\overline{\mathbf{L}}_s^p)^T \overline{\mathbf{L}}_s \quad \mathbf{K}_s^p = (\overline{\mathbf{L}}_s^p)^T (\overline{\mathbf{s}}_{\text{eq}}^p(l) - \overline{\mathbf{s}}_{\text{eq}}^p(l)) \quad (28)$$

The generalization of the Duschinsky transformation to curvilinear modes orthogonal to a LAM allows the calculation of the full vibronic spectrum. Using the factorization introduced in equations 23 and 24, the general sum-over-states expression reported in eq. 2 for the harmonic case can be rewritten as,

$$I(\omega) = \alpha \omega^\beta \sum_{m,j(m)} \left| \langle \overline{\chi}_{0(0)}^{\text{LAM}}(l) \overline{\chi}_0^{N_v-1}(l, \overline{\mathbf{Q}}^p) | \boldsymbol{\mu}^e(l, \overline{\mathbf{Q}}^p) | \overline{\chi}_{j(m)}^{\text{LAM}}(l) \overline{\chi}_m^{N_v-1}(l, \overline{\mathbf{Q}}^p) \rangle \right|^2 \delta \left(\frac{|\overline{E}_{mj} - \overline{E}_0|}{\hbar} - \nu \right) \quad (29)$$

where, for the sake of simplicity, only transitions starting from the vibrational ground state $\overline{\chi}_{0(0)}^{\text{LAM}}(l) \overline{\chi}_0^{N_v-1}(l, \overline{\mathbf{Q}}^p)$ were considered. Furthermore, without loss of generality, the transition dipole moment $\boldsymbol{\mu}^e$ has been expressed in terms of the initial state projected modes $\overline{\mathbf{Q}}^p$. To compute the transition dipole moment, it is convenient to carry out first the integral over the projected modes $\mathbf{Q}^p$, to obtain the LAM-specific transition dipole moment $\boldsymbol{\mu}_m^e(l)$, that is defined as,

$$\boldsymbol{\mu}_{m0}^e(l) = \langle \overline{\chi}_0^{N_v-1}(l, \overline{\mathbf{Q}}^p) | \boldsymbol{\mu}^e(l, \overline{\mathbf{Q}}^p) | \overline{\chi}_m^{N_v-1}(l, \overline{\mathbf{Q}}^p) \rangle \quad (30)$$

For a given value of l , the integral in equation 30 involves only harmonic wavefunctions, thus it can be carried out using the theoretical framework presented in paragraph 2.1, employing either the TI or the TD approach, after expansion of $\boldsymbol{\mu}^e(l, \overline{\mathbf{Q}}^p)$ as a Taylor series in function of $\mathbf{Q}^p$. For the sake of clarity, we will refer to the zero-th and first-order approximations as FC^{N_v-1} and HT^{N_v-1}, in order to avoid confusion with the standard Franck-Condon and Herzberg-Teller models. The second integral required to obtain the full transition dipole moment, and which involves the LAM coordinate l , can be computed numerically, using the diagonal approximation for the DVR basis functions:^{72,73}

$$\langle \overline{\chi}_{0(0)}^{\text{LAM}}(l) | \boldsymbol{\mu}_m^e(l) | \overline{\chi}_{j(m)}^{\text{LAM}}(l) \rangle = \sum_{k=1}^{N_{\text{DVR}}} \overline{\mathbf{C}}_{j(m),k}^{\text{LAM}} \overline{\mathbf{C}}_{0(0),k}^{\text{LAM}} \boldsymbol{\mu}_m^e(l_k) \quad (31)$$

where $\overline{\mathbf{C}}^{\text{LAM}}$ and $\overline{\mathbf{C}}^{\text{LAM}}$ are the matrix of the eigenfunctions of $\mathcal{H}^{\text{vib}}$ expressed in terms of the DVR basis set. As anticipated above, equation 31 holds only if the same DVR basis set is employed for the expansion of the LAM wavefunctions of the two electronic states, and therefore if the same curve $\mathbf{a}_{\text{LAM}}(l)$ is used to define the LAM in the two electronic states.

To use equation 31, the transition dipole moment μ_{m0}^e must be computed at each point of the DVR grid ($I_1, \dots, I_H$). Those values can be obtained, for each final state $\bar{\chi}_{m(0)}^{N_v-1}(l, \bar{\mathbf{Q}}^p)$, from the transition dipole moment μ_m^e at each point of the QM grid, arising from the scan calculation ($\tilde{I}_1, \dots, \tilde{I}_H$), and fitting those values using the B-spline representation as already done for the electronic energies. The matrices of the eigenfunctions $\bar{\mathbf{C}}^{\text{LAM}}$ and $\bar{\mathbf{C}}^{\text{LAM}}$ are obtained by diagonalization of the Hamiltonian given in equation 24 in the DVR basis set. To compute the second term of the potential energy ($E_k^{N_v-1}(l)$ in equation 24), arising from the vibrational energy of the “ $N_v - 1$ ” harmonic modes, the projected frequencies $\omega_i^p(l)$ are fitted using B-splines, and the term is computed, for each value of l , from equation 22. It is important noting that, due to the presence of this second term, a different Schrödinger equation is obtained for each final state $\bar{\chi}_m^{N_v-1}(l, \bar{\mathbf{Q}}^p)$.

The general theory outlined above can be simplified to reduce the overall computational cost. Significant saving is achieved by neglecting the dependence on l of the vibrational energy of the “ $N_v - 1$ ” harmonic modes $\mathbf{Q}^p$. Under this approximation, $E_k^{N_v-1}(l)$ can be approximated as $E_k^{N_v-1}(l_0)$ in equation 24, where l_0 is the IRC parameter of some reference geometry. The vibrational Schrödinger equation associated to the LAM, given in equation 24, can then be rewritten as,

$$[\mathcal{T}(l) + \mathcal{V}(l)] \chi_{i(k)}^{\text{LAM}}(l) = (E_{i(k)}^{\text{tot}} - E_k^{N_v-1}(l_0)) \chi_{i(k)}^{\text{LAM}}(l) \quad (32)$$

where the energy E_i of the i -th state of the LAM does not depend anymore on k . Using this approximation, equation 29 can be rewritten as follows:

$$I(\omega) = \alpha \omega^\beta \sum_{m,j(m)} \left| \langle \bar{\chi}_{0(0)}^{\text{LAM}}(l) | \mu_m^e(l) | \bar{\chi}_{j(m)}^{\text{LAM}}(l) \rangle \right|^2 \delta \left(\frac{|\bar{E}_m + \bar{E}_j - \bar{E}_0|}{\hbar} - \omega \right) \quad (33)$$

This equation can be further simplified within the Franck-Condon approximation for the $N_v - 1$ orthogonal modes $\mathbf{Q}^p$, so that $\mu_m^e(l)$ can be rewritten,

$$\mu_m^e = \mu^e(l, \mathbf{Q}_{\text{eq}}^p) \times \langle \bar{\chi}_m^{N_v-1}(l, \bar{\mathbf{Q}}^p) | \bar{\chi}_0^{N_v-1}(l, \bar{\mathbf{Q}}^p) \rangle \quad (34)$$

where $\mu^e(l, \mathbf{Q}_{\text{eq}}^p)$ is the transition dipole moment computed, for each value of l , at the equilibrium configuration of the orthogonal modes. Even if this simplification does not give any significant computational saving, it can be used to separate the contributions of the LAM from the ones of the orthogonal modes to the transition dipole moment. To further simplify the sum-over-states expression in equation 33, the dependence of the nuclear wavefunctions $\bar{\chi}_0^{N_v-1}(l, \bar{\mathbf{Q}}^p)$ and $\bar{\chi}_m^{N_v-1}(l, \bar{\mathbf{Q}}^p)$ on the IRC parameter l can also be neglected, leading to the final result,

$$I(\omega) = \alpha \omega^\beta \sum_{m,j(m)} \left| \langle \bar{\chi}_{0(0)}^{\text{LAM}}(l) | \mu_m^e(l) | \bar{\chi}_{j(m)}^{\text{LAM}}(l) \rangle \right|^2 \times \\ \left| \langle \bar{\chi}_m^{N_v-1}(l, \bar{\mathbf{Q}}^p) | \bar{\chi}_0^{N_v-1}(l, \bar{\mathbf{Q}}^p) \rangle \right|^2 \delta \left(\frac{\bar{E}_m + \bar{E}_j - \bar{E}_0}{\hbar} - \omega \right) \quad (35)$$

which is equivalent to the expression used in previous works.^{8,87}

3 Computational details

All computations have been performed with a modified version of the GAUSSIAN suite of quantum chemical programs⁸⁸ extended to support the theoretical framework presented in section 2. Calculations were performed at the density functional theory (DFT) level and its time-dependent extension (TD-DFT) using the B3LYP exchange-correlation functional⁸⁹ in conjunction with the SNSD basis set,⁹⁰ obtained by adding to the 6-31G(d,p) basis set a minimal number of core-valence (one *s* function on all non-hydrogen atoms) and diffuse (*s,p,d* on non-hydrogen atoms and *p* on hydrogen atoms) functions optimized specifically for global hybrid functionals.^{91,92} Ionization energies of NH₃ have been computed at the - SCF level, therefore computing them as difference between the electronic energies of the neutral and of the cationic species, both computed at the DFT level. Ionization energies were also calculated using electron propagator theories (EPT) as poles of the one-particle Green function. Among them, the non-diagonal second-order approximation of the propagator (NR2) was employed, whose reliability has been shown in a recent benchmark.⁹³ EPT calculations have been performed using the implementation available in the development version of GAUSSIAN, and additional details can be found in refs.^{94,95}

Vibronic simulations at the harmonic level have been performed employing our time-independent implementation^{8,9,37} which uses a class-based prescreening scheme to select *a priori* the most intense vibronic transitions (additional details about the prescreening scheme can be found in refs.^{47,96}). If not specified otherwise, the standard parameters of the class-based prescreening scheme, which can be found, for example, in refs.^{8,17} have been used. In all cases, temperature effects have been neglected. To designate the vibronic model employed in the simulation, the approximation for the PES (VG, VH, AS, AH) and the approximation of the electronic transition dipole moment (FC, FCHT) will be combined in a single acronym (as, for instance, AH|FC).

Regarding internal coordinates, PICs have been generated from the molecular topology as described in ref.¹⁷ The redundant Wilson **B** matrices have been computed using analytical expressions for bond lengths, valence, out-of-plane and dihedral angles.^{58,97} In the calculation of the SVD of the redundant **B** matrix to generate DICs, a threshold of 10⁻⁵ has been used to select the singular vectors corresponding to non-zero singular values.

IRC calculations on cyclobutanone have been performed using the Hessian-based Predictor-Corrector integrator introduced in refs.^{98,99} as implemented in GAUSSIAN,¹⁰⁰ using a step size of 0.05 Bohr, for a total number of 27 points. The fitting of the PES to a double Morse

potential has been done by using a Levenberg-Marquardt algorithm.⁷⁹ For the B-spline fitting, not-a-knot boundary conditions⁷⁹ were used in all cases.

4 Applications

4.1 Photoelectron spectrum of ammonia

A first application is the photoelectron spectrum of ammonia for the $\tilde{X}^2A_2'' \leftarrow \tilde{X}'A_1'$ electronic transition, corresponding to the removal of one electron from the HOMO. The difference between the equilibrium geometries of the ground neutral and cationic states of ammonia is large, with the former being pyramidal and the latter planar. Therefore, a LAM along the umbrella inversion coordinate occurs upon ionization. This can be inferred from the shape of the two PESs as well, since the one of the neutral state is a double-well, whereas the one of the cationic state shows a single minimum. As a result, the experimental photoelectron spectrum (reported in ref.¹⁰¹ and, in a more recent work, in ref.¹⁰²), shows a large progression of the vibrational excitations associated to the umbrella inversion mode. Consequently, the photoelectron spectrum of ammonia is a classical test case for methods developed to treat accurately LAMs. As discussed in ref.¹² the simplest vibronic models (harmonic and Franck-Condon approximation, neglect of mode-mixing effects) fail in this case for two reasons: the position of the maximum of intensity for the progression of the umbrella mode is incorrect, and spurious progressions, not detected in the experimental spectrum, are present in the theoretical one. Inclusion of second-order terms in the expansion of the transition dipole moment¹⁰³ improves only slightly the overall bandshape, without removing the spurious progressions. In refs.^{104,105} it has been shown that the description of the progression involving the inversion mode can be improved by including anharmonic effects. However, the theoretical models presented in those works were monodimensional, and couplings between the inversion mode and the other modes were neglected *a priori*. Improvements have been proposed more recently by Peluso and co-workers,¹² where it was established that a significant coupling between the inversion and the symmetric stretching mode is present, and therefore at least two-dimensional anharmonic approaches are needed in cartesian coordinates. On the other hand, if curvilinear internal coordinates are adopted,^{51,106} the coupling between the symmetric stretching mode and the other modes is strongly reduced, so that the bandshape is significantly improved even at the harmonic level. Still, by neglecting anharmonic effects, discrepancies are present with respect to the experimental data. In order to overcome this limitation, our hybrid DVR-harmonic approach will be used. It should be remarked that several types of simulations are already available in the literature, based either on semi-classical¹⁰⁷ or full-quantum dynamics^{108,109} approaches. However, their computational cost is rather high, and their extension to larger-size systems is less straightforward than our DVR-based approach.

Before comparing theoretical and experimental results, ammonia has been also used to check the numerical stability of the DVR-based approach with respect to the graining of the two grids used in the scan and in the variational calculation. In table 1, the energies of the five lowest vibrational levels of the inversion mode of ammonia, computed with different grids, are reported. The PES along the umbrella mode has been computed from a non-

relaxed scan along the inversion mode from 50° to 130° (therefore using the NR-ICPH model). The results reported in table 1 show that, for a given step-size and a given number of points of the non-relaxed scan (which gives a unique representation of the PES in terms of B-splines), 150 DVR basis functions (corresponding to a grid spacing of 0.53°) are sufficient to reach a convergence of the energy levels within 1 cm^{-1} . On the other hand, a significantly larger step-size, of 4° , can be safely used in the scan, where discrete geometries are taken at regular intervals along the large-amplitude coordinate, to reach convergence in the B-spline fitting. Those findings are in line with our discussion in the theoretical section, and confirm that a fitting step preceding the DVR calculation significantly improves the efficiency of the simulation. The last column of table 1 contains the energies of the 5 lowest vibrational states for the ground, neutral state of ammonia computed after a relaxed scan of the PES along the inversion coordinates, therefore using the ICPH model. The difference between the frequencies computed within the ICPH and NR-ICPH is, in all cases, above 15 cm^{-1} , with a maximum reached for the highest-frequency modes, where it is above 100 cm^{-1} . This shows that the impact of geometrical relaxation along the LAM can be comparable to anharmonic effects.

As already stated, the PES of the ground, neutral state is a double-well potential, where the planar configuration corresponds to a saddle point, and thus the RPH framework can be employed too. Ammonia is also an ideal case to test the extrapolation procedure coupled to RPH since, due to the symmetry of the system, only one degree of freedom (the N–H distance) needs to be optimized along the scan, and therefore RPH should be equivalent to ICPH. The vibrational energies computed using ICPH and RPH with different extrapolation schemes are reported in table 2. Based on the previous results, 150 DVR basis functions have been used for each simulation and, for ICPH, a step-size of 4° has been employed. The results of the simulation show that, if the extrapolation is performed including only the points obtained from an IRC calculation (second column of table 2), large deviations, above 60 cm^{-1} in all cases, from the frequencies computed at the ICPH level are observed. A significant improvement in the quality of the results can be obtained by computing the electronic energies for geometries beyond the minima, following the normal mode correlating with the IRC coordinate (which is in this case the umbrella-inversion mode). The discrepancy with the ICPH results decreases, and is approximately 10 cm^{-1} if 8 points (4 for each side of the IRC) are added. From those results, it is clear that extrapolation is mandatory to minimize the error for a given number of scan points.

Based on the analysis reported above, vibrational properties for the cationic state have been computed too, using the σ -SCF approach for the ionization energies. In the theoretical section it was stated that the anharmonic model presented here is effective only if internal coordinates are adopted to minimize the coupling between the LAM and the other modes. This is the case for the photoelectron spectrum of ammonia, as shown in figure 3, where the experimental¹⁰² and theoretical spectra computed at the AH|FC level using cartesian and DICs are reported. The experimental band-shape, which is characterized by a single, well-resolved vibronic progression, corresponding to excitations of the inversion mode, is reproduced qualitatively only using DICs, while the spectrum obtained in cartesian coordinates has a very different and broader shape. As already discussed in ref.,¹² the presence of unphysical couplings between the symmetric stretching and the inversion mode

in the definition of $\mathbf{J}_x$ generates those progressions, leading to a poor reproduction of the band-shape. Even using DICs, despite a general improvement in the reproduction of the experimental data, the spacing and relative intensity of the bands is still not reproduced accurately, due to strong anharmonic effects. To further improve the accuracy of the simulation, the DVR-based scheme outlined above is thus necessary.

As already explained in section 2, when computing vibronic spectra using the DVR-approach within the ICPH framework, one of the two states involved in the transition must be chosen as reference for the scan. In figure 4, the theoretical spectra obtained using the neutral and cationic states as reference in the relaxed scan calculations are reported. This comparison shows that the choice of the reference state has a minor impact on the reproduction of the vibronic band-shape. In fact, for most transitions, the difference in frequencies is below the resolution of the experimental spectrum, and only slightly detectable for the higher-energy transitions. Marginally larger discrepancies are found for intensities, with those of the lower-energy bands are overestimated with respect to the experimental data using the optimized geometries of the neutral state. Using the cationic state as reference, a better agreement is reached. To understand this behavior, it should be recalled that, when temperature effects are neglected, only the energy and wavefunction of the vibrational ground state of the initial electronic state is needed to compute the Franck-Condon integrals, whereas excited vibrational levels of the final state are still needed. Since, as remarked above, the PES of one of the two states has to be described with lower accuracy, the less impacting choice is to perform the optimized scan using the final state as a reference. Still, both theoretical spectra reported in figure 4 are significant improvements over the harmonic spectrum in figure 3. To further check the reliability of the theoretical results, the spectrum has been computed with ionization energies from the NR2 approach, 93,110 using the geometries computed at the DFT level. As shown in figure 4, the results obtained using this more accurate electronic-structure approach are in agreement with the ones obtained at the ω -SCF level. Therefore, the discrepancies with the experimental spectrum are related primarily to the choice of the reference geometry for the scan.

4.2 LIF spectrum of phenylanthracene

The second system studied here is 9-phenylanthracene, represented in figure 2) and labeled in the following as 9PA. 9PA belongs to a class of molecules characterized by two aromatic rings connected by a formally single bond, whose spectroscopic properties are strongly related to the torsion about this bond. For this reason, high-resolution electronic spectroscopies, both for absorption and for emission processes, have been widely used to characterize the torsional potential for ground and excited electronic states.^{111,112} This is the case also for 9PA, which has been recorded at high-resolution over the energy range associated to vibrational transitions involving the torsional motion.¹¹³ From a computational point of view, while a wide range of theoretical approaches have been used to model the potential energy surface along the torsional angle for those systems,^{114–116} characterization of the vibrational and vibronic properties at the anharmonic level has been scarce. Moreover, vibrational levels associated to the torsional mode have generally been calculated at the anharmonic level from variational approaches based on the Fourier basis set,^{18,19,21,50} but relying on a free rotor-like Hamiltonian, where the coupling between the

LAM and the other degrees of freedom was neglected. Here, the more complete, RPH-based model described above will be employed.

As already discussed in previous theoretical works,^{117,118} the first band of the absorption spectrum can be assigned to the $S_1 \leftarrow S_0$ electronic transition, which is bright and involves molecular orbitals mainly localized on the anthracene group. As suggested by the analysis of the high-resolution OPA spectrum of 9PA, and further confirmed by CASSCF calculations,¹¹⁷ the dihedral angle between the phenyl and the anthracene moieties is 90° in the ground state and about 55° in the S_1 one. To further check those results, the potential energy surface along the dihedral angle of 9PA has been computed, choosing both the S_0 and the S_1 electronic states as reference. The results shown in figure 5 are in agreement with the experimental findings, since the PES has a single minimum in the S_0 state, whereas a double-well is present in the excited state. As expected, the height of the well in the S_1 state is lower if S_1 is taken as reference in the relaxed scan calculation and amounts to 233 cm^{-1} , in excellent agreement with the experimental value of 243 cm^{-1} .¹¹³ In contrast, use of S_0 as reference for the optimized scan leads to a barrier height of 293 cm^{-1} . This difference has a significant impact on the computed OPA spectrum along the torsional profile, reported in figure 6. In fact, with the optimized scan based on the S_0 state used for the definition of the LAM, the most intense bands of the computed spectrum result shifted toward higher energies with respect to the experimental data. On the other hand, with the relaxed scan on the S_1 state, the agreement improves to the point that the most intense bands of the spectrum can be straightforwardly assigned. Up to now, all simulations have been performed at the FC level, therefore neglecting the variation of the transition dipole moment along the LAM. As shown in the lower panel of figure 5, the value of the transition dipole moment is minimized for a torsional angle of 90° , and grows along the LAM, therefore its variation should be taken into account in the vibronic simulations. The results in figure 6 show, however, that this has only a minor impact on the computed spectrum, which is reproduced satisfactorily already at the FC level.

4.3 A more challenging case: the absorption spectrum of cyclobutanone

The two molecules used as test-cases in the preceding sections were characterized by LAMs (torsion and umbrella inversion) which can be described using well-defined linear combinations of primitive internal coordinates. However, for more complex LAMs, such a simple description is usually impossible. For example, a large class of cyclic molecules, which are planar in the ground state and undergo a deformation upon electronic excitation, cannot be described trivially in terms of PICs.^{119,120} In those cases, the LAM can be efficiently described using the RPH model, since the planar configuration is a transition state for the electronic excited state, so that the LAM can be parametrized using the intrinsic reaction path connecting the transition state to a minimum.

The high-resolution experimental spectra of a wide range of cyclic compounds have been recorded by Laane and co-workers, both within IR and UV-vis energy ranges, so that vibronic transitions can be singled out.^{23,121,122} In most cases, the interpretation of these experimental data is performed using semi-empirical mono- and bi-dimensional Hamiltonians for the PES along the LAM, parametrized by fitting the eigenvalues of the

Hamiltonian to the experimental transition energies.^{23,122} Those analyses illustrated the fact that monodimensional Hamiltonians can be satisfactory only if applied to represent the energy levels of a narrow sample of cases, such as four-membered rings¹²³ and five-membered rings with a double bond.^{124,125} For more complex systems,¹²⁶ a multidimensional Hamiltonian must be used to obtain reliable results. In any case, characterizations of those experimental data using PES obtained from *ab initio* calculations, and not fitted to experimental data, are scarce in the literature. Here, we will focus on the simulation of the one-photon absorption spectrum of cyclobutanone (represented in figure 2) for the $S_1 \leftarrow S_0$ ($n \rightarrow \pi^*$) transition, using the experimental data reported in refs.^{123,127}

The OPA spectra of cyclobutanone for the $S_1 \leftarrow S_0$ transition computed at the harmonic level, using the AH|FC and AH|FCHT models in cartesian and internal coordinates, are plotted in figure 7. The main vibronic progression, characterized by bands with a constant spacing of $\approx 300 \text{ cm}^{-1}$, is due to the ring-inversion mode, which corresponds to the LAM. As expected, the band-shape is narrower in DICs than in cartesian coordinates, due to the reduced coupling between the LAM and the other modes. Furthermore, the inclusion of HT effects is relevant, especially when internal coordinates are used, and results in a shift of the spectral maximum towards higher energy. However, in both cases, the description of the vibrational states involving the LAM is insufficiently accurate. In figure 8, the theoretical OPA spectrum, broadened by means of Gaussian functions with half-widths at half-maximum (HWHMs) of 10 cm^{-1} , is compared to the experimental, high-resolution laser-induced fluorescence (LIF) spectrum, taken from ref.¹²³ For both cartesian and internal coordinates, the vibronic progression of the LAM is reproduced incorrectly, and the intensity of the bands in the computed spectra increases constantly with the energy, whereas, in the experimental data, it reaches a maximum for the fourth band and then decreases.

In order to improve the accuracy of the simulation, the vibronic spectrum has been simulated using the anharmonic model described above. For the two previous test cases (ammonia and PA), the vibronic spectrum was simulated only in the region where overtones of transitions associated to the LAM were predominant, so couplings with the other modes could be neglected in the simulation. However, in the experimental OPA spectrum of cyclobutanone, 123 bands involving also the other modes are present, thus the full-dimensional spectrum will be computed using the approach presented in the theoretical section. As noted before, the description of the LAM as a fixed linear combination of primitive internal coordinates is less trivial than for the previous systems, so the RPH framework will be employed. Furthermore, the S_1 state, with a saddle point for the planar configuration, has been taken as reference in the IRC calculation, and the same geometries have been used to compute the S_0 PES. The PES along the LAM, shown in figure 9, has a significantly different shape in the ground and excited electronic states. This difference has a significant impact on the pattern of the vibrational energy levels, since in the first case they are nearly equispaced, and the spacing decreases slowly with the increasing energy. On the other hand, for the double-well potential, two different regions can be identified. For vibrational energies below the barrier of the double-well (which is approximately 1300 cm^{-1}), couples of nearly-degenerate states are present, which are symmetric and antisymmetric with respect to the planar configuration, respectively. For energies comparable and above the barrier, the splitting between nearly-degenerate states increases. It is noteworthy that this trend cannot be reproduced, even at a

qualitative level, using an harmonic description, where the spacing is constant. When the coupling between $N_v - 1$ harmonic modes is taken into account, the vibronic progression involving vibrational states where only the LAM is excited can be computed at the lowest level of approximation by neglecting three effects, namely the variation of the ZPVE based on the projected harmonic modes along the LAM, the variation of the transition dipole moment along the LAM and the change of the intensity of the $\langle \bar{0} | \bar{0} \rangle$ integral for the harmonic modes. By neglecting all those effects, the variational calculation is performed directly on the PES arising from the IRC calculation, and the intensity of the transitions is given by FC integrals between LAM vibrational wavefunctions. As shown in figure 10, the agreement between the theoretical spectrum computed within those approximations and the experimental data is improved with respect to the harmonic result, but is still not satisfactory, especially for the higher-energy transitions. However, inclusion of the variation of the transition dipole moment along the LAM (green line in figure 10) results in a significant gain in accuracy. To explain this difference, it should be remarked that, in the FC simulation, considering the symmetry of the system, only transitions to states which are symmetric with respect to the top of the well have non-null intensity, since the initial, ground state is symmetric as well. On the other hand, in the HT simulations, only transitions to antisymmetric states are allowed, since the transition dipole moment is antisymmetric. For the lowest-energy transitions, the difference is minimal, since the couples of symmetric/antisymmetric states are nearly-degenerate. On the other hand, for higher-energy states, as the splitting increases, such a constraint has a significant impact on the computed band-shape. To refine further the quality of the theoretical results, the other two effects, namely the variation of the intensity of the 0-0 transition and of the ZPVE based on the projected harmonic modes along the LAM, need to be included (see lower panel of figure 10). As expected, inclusion of the variation of the intensity of the 0-0 transition associated to the projected modes Q^p (spectrum in solid, blue line) changes only the relative intensity of the bands but not their positions. More precisely, the relative intensities of the most intense bands are improved, even if those of the two lowest-energy bands are still underestimated. Inclusion of the variation of the ZPVE leads to a better agreement in the band-positions with respect to experiment, with the position of the first 5 bands reproduced with an accuracy within 10 cm^{-1} . Finally, the full-dimensional OPA spectrum computed using the hybrid harmonic-DVR scheme is reported in figure 11. The transitions involving the $N_v - 1$ harmonic modes have been simulated with the VH model. For each geometry along the IRC, all $N_v - 1$ projected harmonic frequencies are positive, and therefore all modes have been included in the simulation. The overall band-shape is reproduced correctly as well, even if discrepancies are still present in the intensities of several bands between 31400 and 31800 cm^{-1} . However, those bands correspond to transitions to vibrational states, with energy comparable to the height of the well, and thus their intensity strongly depends on the accuracy in the reproduction of this height. For this reason, to further improve the accuracy of the results, more refined electronic structure methods would be necessary in the calculation of the PES.

5 Conclusions

This work presents a new theoretical method for the simulation of vibronic properties of medium- to large-size flexible systems including anharmonic effects. The method is based on an hybrid scheme, where a single degree of freedom, corresponding to the large-amplitude motion accompanying the electronic transition, is treated at a full-variational, anharmonic description, whereas the other modes are described as harmonic. Within this approach, internal coordinates are employed to minimize the coupling between the LAM and the other degrees of freedom. A scan calculation is used to obtain the potential energy surfaces of the two electronic states along the LAM, and transition properties between the vibrational levels of the two electronic states are computed using anharmonic wavefunctions for the LAM, obtained from the variational calculation. Either the reaction path Hamiltonian or the internal coordinates path Hamiltonian model can be used for the definition of the coordinate describing the LAM, allowing the support of arbitrarily complex deformations. Unlike most of the models available in the literature, the variations of the harmonic normal modes along the LAM are properly taken into account within an adiabatic picture.^{27,28} The description of the harmonic degrees of freedom is based on the models developed for fully harmonic simulations, therefore supporting both adiabatic and vertical models with the possible inclusion of mode-mixing and Herzberg-Teller effects. The application of this model to several test-cases shows that this hybrid scheme is effective not only for standard deformations (such as inversions and torsions along a dihedral angle) but also for less trivial, large-amplitude motions, such as ring deformations. The overall procedure is particularly interesting since it gives the possibility to simulate effectively a whole class of spectra for a limited increase of the computational cost.

The framework presented here can be improved in several respects. First, for specific kinds of deformation, it is not possible to associate the LAM to a single mode, decoupled from the others. The monodimensional, hybrid scheme would be inaccurate for those systems, since multidimensional variational models would be required. The theoretical framework presented here can be generalized to multiple dimensions using the vibrational Hamiltonian already used for the reaction surface (RSH)^{67,84} and reaction volume (RVH)^{128,129} Hamiltonian models, which are the extensions of RPH to 2 and 3 dimensions. Those models are however much less studied than RPH, and have been applied up to now only to cartesian coordinates. The generation of the geometries for the scan calculation is also more cumbersome than for the monodimensional case, since extensions of IRC algorithms to multiple dimensions have not been studied, up to our knowledge. Finally, the parametrization of multidimensional PESs is less trivial than in the monodimensional case,^{68,69} and leads to a more complex form for the kinetic energy operator.

Next, the effectiveness of the hybrid DVR-harmonic monodimensional model can be increased with the computation of properties in addition to the transition dipole moment, like magnetic and higher-order properties. This would give access to the simulation of chiroptical^{32,130} and resonance⁴⁹ spectroscopies. Finally, the integration of the present model with the ones developed recently by some of us to compute rates of different non-adiabatic phenomena at the harmonic level,^{131,132} would give access to the evaluation of anharmonic effects also for those phenomena.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Graphical representation of the extrapolation procedure used for RPH. In the first two steps (labelled as 1 and 2) IRC calculations are used to compute PES between the saddle point and each of the two minima (black crosses) of the double well, which is then fitted using a B-spline representation (solid, green line). Then (steps 3 and 4) the PES beyond the stationary points (solid, red line) is obtained through a relaxed scan along the mode associated to the LAM (gray crosses). To limit the number of points of the scan calculation (steps 5 and 6), the PES can be extrapolated by fitting it to a double Morse potential (dashed, black line).

Note that, for symmetric double-well potentials, steps 2, 4 and 6 are equivalent to 1, 3 and 5, and therefore can be avoided.

(a)

(b)

Figure 2.
Molecular structures of phenylanthracene (a) and cyclobutanone (b).

Figure 3.

Experimental¹⁰² (dashed, black line) and theoretical photoionization spectra of the

$\tilde{X}^2A_2'' \leftarrow \tilde{X}'A_1'$ transition of ammonia computed at the AH/FC level in cartesian (solid, red line) and delocalized internal (solid, green line) coordinates. Lorentzian broadening functions with HWHM of 50 cm^{-1} have been used to simulate broadening effects.

Figure 4.

Theoretical photoionization spectrum of the $\tilde{X}^2A_2'' \leftarrow \tilde{X}'A_1'$ transition of ammonia computed including only overtones of the inversion mode and using the variational, DVR-based approach to compute energies and intensities. The theoretical spectra have been obtained using the neutral (left panel) and cationic (right panel) electronic state as a reference for the scan calculation. Ionization energies have been computed at the Δ SCF (green, solid lines) and NR2 (red, solid lines) level of theory. The experimental spectrum, taken from ref.,¹⁰² is reported as well, and has been shifted by 0.05 eV toward lower energies to facilitate the comparison with the theoretical results. Lorentzian functions with HWHM of 50 cm^{-1} have been used to simulate the broadening effects.

Figure 5.

Upper panel: plot of the PES along the torsional angle between the two aromatic rings of 9PA computed within the ICPH framework using the S_0 (dashed lines) or the S_1 (solid line) electronic state as reference. Electronic structure calculations have been performed at the B3LYP/SNSD level.

Lower panel: plot of the norm of the transition dipole moment of the $S_1 \leftarrow S_0$ transition along the torsional mode of 9PA. The relaxed scan calculation has been performed on the S_1 electronic state.

Figure 6.

Experimental¹¹³ (dashed, black line) and theoretical OPA spectra for the torsional mode of 9PA, computed using the ICPH model and using the S₀ (solid, red line) and the S₁ (solid, green line) electronic state as reference in the scan calculation and by neglecting the variation of the transition dipole moment along the LAM. Electronic structure calculations have been performed at the B3LYP/SNSD level. The experimental data, taken from ref.,¹¹³ is also reported.

Figure 7.

OPA spectrum of the $S_1 \leftarrow S_0$ transition of cyclobutane computed at the AH/FC (dashed lines) and AH/FCHT (solid lines) level using cartesian (red lines) and delocalized internal (green lines) coordinates at the harmonic level. Gaussian functions with HWHMs of 50 cm^{-1} have been used to reproduce the broadening effects.

Figure 8.

Experimental¹²³ and theoretical OPA spectra of the $S_1 \leftarrow S_0$ transition of cyclobutane computed at the AH/FCHT level using cartesian (red line) and delocalized internal (green line) coordinates at the harmonic level. Gaussian functions with HWHMs of 10 cm⁻¹ have been used to reproduce the broadening effects.

Figure 9.

Graphical representation of the PES along the ring inversion mode for the S_0 (left panel) and S_1 (right panel) electronic states of cyclobutanone, computed at the B3LYP/SNSD level of theory and using the RPH framework. The vibrational levels and wavefunctions, computed using the variational, DVR-based approach, are also reported.

Figure 10.

Experimental¹²³ (dashed, black line) and theoretical OPA spectra of the $S_1 \leftarrow S_0$ transition of cyclobutanone computed at the B3LYP/SNSD level, using the RPH model and including vibronic transitions involving only the ring-inversion mode. The spectra obtained by neglecting the variation of the transition dipole moment along the LAM (solid, red line) and including it (solid, green line) are reported. To facilitate the comparison between theoretical and experimental results, the theoretical spectra have been shifted to match the experimental value of the energy of the 0-0 transition.

Figure 11.

Experimental¹²³ (dashed, black line) and theoretical OPA spectrum for the $S_1 \leftarrow S_0$ transition of cyclobutanone computed at the B3LYP/SNSD level, using the RPH model, together with the hybrid DVR-harmonic model. To facilitate the comparison between theoretical and experimental results, the theoretical spectra have been shifted to match the experimental value of the energy of the 0-0 transition.

Table 1

Vibrational energies of the 5 lowest-energy vibrational states of ammonia computed using the DVR-based approach with different step sizes in the PES scan calculation (expressed in degrees) and with a different number of basis functions. The energies are reported in wavenumbers. All electronic structure calculations have been performed at the B3LYP/SNSD level. In all cases, non-relaxed scans have been performed, except for the last column, where the results issuing from a relaxed scan are reported.

		Number of DVR basis functions			
		100	150	200	150(rel)
Scan step-size	2°	519.69	521.58	521.79	504.32
		520.67	522.56	522.77	505.72
		1451.14	1453.05	1453.27	1392.42
		1496.07	1497.99	1498.21	1449.91
		2106.84	2108.78	2109.02	2021.75
	4°	519.75	521.65	521.86	504.36
		520.74	522.63	522.84	505.77
		1451.28	1453.19	1453.41	1392.50
		1496.28	1498.20	1498.42	1450.05
		2107.04	2108.98	2109.22	2021.88
	8°	520.25	522.18	522.40	505.61
		521.25	523.17	523.39	507.03
		1451.76	1453.70	1453.93	1393.91
		1497.16	1499.10	1499.34	1451.95
		2107.44	2109.41	2109.67	2023.04
	16°	521.48	521.49	522.14	499.87
		522.54	522.55	523.21	501.34
		1443.77	1443.79	1444.46	1369.87
		1495.29	1495.32	1495.99	1433.99
		2071.20	2071.26	2071.94	1970.31

Table 2

Vibrational energies of the 5 lowest-energy vibrational states of ammonia computed within the ICPH (column 1) and RPH frameworks (column 2-7). For RPH calculations, calculations have been performed adding scan points beyond the minima (the number of the additional point is reported in the "Add. points" row). All electronic structure calculations have been performed at the B3LYP/SNSD level.

LAM model		ICPH	RPH	RPH	RPH	RPH	RPH	RPH (no extr.)
Add. points			0	2	4	6	8	8
Vibr. level	n=0	504.36	573.57	551.37	527.66	508.67	496.74	697.33
	n=1	505.77	575.61	553.22	529.27	510.14	498.10	734.43
	n=2	1392.50	1509.51	1478.74	1446.97	1419.36	1399.21	1687.33
	n=3	1450.05	1605.41	1564.33	1521.50	1486.44	1460.06	1904.33
	n=4	2021.88	2188.32	2145.46	2105.10	2070.83	2045.91	2558.45