On the application of canonical perturbation theory to floppy molecules

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Canonical perturbation theory (CPT) is a powerful tool in the field of molecular physics. It consists of a series of coordinate transformations aimed at rewriting the Hamiltonian in a simpler form without modifying the geometry of the phase space. The major achievement of CPT is the straightforward derivation of relations between the physically meaningful parameters of potential energy surfaces and the coefficients of the so-called effective Hamiltonians. While most of the studies performed up to date deal with surfaces expanded in polynomial series around a single minimum, CPT has also been applied to mixed polynomial/trigonometric expansions in the treatment of torsions. In this latter case, however, the accuracy of CPT has not been verified. The goal of this article is to suggest some modifications of the procedures, which allow for the successful application of CPT to floppy molecules with several equilibrium positions and nonpolynomial expansions. The levels belonging to all the wells or located above the saddle points are satisfactorily reproduced by the perturbative Hamiltonian. More precisely, the vibrational modes are sorted into two categories, namely oscillator-like ones and hindered-rotor-like ones. The application of CPT enables the expression of the Hamiltonian in terms of the good quantum numbers and/or classical constants of the motion associated with the oscillator-like modes. The perturbative Hamiltonian then acts on the reduced dimensional space of the hindered-rotor-like modes. The validity and accuracy of this approach are tested on two-dimensional and three-dimensional models mimicking, respectively, nonlinear and linear HCN. © *2000 American Institute of Physics.*
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I. INTRODUCTION

Since the pioneering work of Nielsen[1] in the early fifties, canonical perturbation theory (CPT) has been a powerful tool in the field of molecular physics. Whether based on the original quantum approach due to Van Vleck,[2–8] the classical method developed by Birkhoff[9] and later extended by Gustavson[10] (see also Refs. 11 and 12 for a good description), or the more recent classical procedures based on Lie algebra,[13–19] the purpose for applying CPT is always the same: the goal is to find a sequence of canonical (or unitary) transformations of the coordinates, which help write the Hamiltonian in a simpler form. Most of the time, this is obtained by finding almost conserved quantum numbers or approximate classical constants of the motion and in expressing the Hamiltonian in terms of these quantities. The advantage for doing so is twofold. First, the solutions (eigenvalues and wave functions) can be obtained with sufficient accuracy using a significantly smaller basis set than is needed to obtain the solutions in the original representation. More important, however, is the fact that the conserved quantities allow for a much simpler and deeper study of the dynamics (bifurcations, intramolecular vibrational energy redistribution (IVR), chaos, etc.) of the system, especially when associated with the so-called Einstein–Brillouin–Keller (EBK) semiclassical quantization rules.[20–22] It is also to be noted that even in the cases where the perturbation scheme is not effec-

tively applied to the studied system, the so-called ''spectroscopic Hamiltonians,'' whose forms are just the expected results of CPT, provide remarkably accurate fits over large energy ranges. The most well-known examples of such spectroscopic Hamiltonians are the Dunham expansion, the Fermi resonance Hamiltonian, and the Darling–Dennison resonance Hamiltonian (see, for example, Refs. 23–35 for some studies dealing with SO_2, NO_2, CO_2, CS_2, HOCl, CHD_3, and H_2S).

Up to now, CPT has been shown to work for some low-order polynomial surfaces, which are expected to model atomic (see, for example, Ref. 36) or molecular systems (see, for example, Refs. 11,37–42) from the regular up to the strongly chaotic regions, and for a variety of accurate potential energy surfaces (PES) for molecules like H_2O, SO_2, CO_2, HCN, HCP, C_2H_2, H_2CO, and AlF_3 obtained either from fits or *ab initio* calculations (see, for example, Refs. 7,8,43–53). In each case, the energy levels and wave functions of the exact and perturbative Hamiltonians were shown to be in good agreement. The procedure in the examples quoted above involves (i) expansion of the PES in Taylor series around the minimum energy configuration, (ii) application of CPT to the polynomial expression thus obtained, and (iii) assumption that the zero-order Hamiltonian can be taken as the sum of the harmonic oscillators associated with each degree of freedom. This procedure, however, clearly does not work for floppy molecules, that is, for molecules with several equilibrium positions separated by barriers which are not too high. The principal reason is that the mo-

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tion is too different from one well to another to be described by a single oscillator. For example, the studies dealing with HCN mentioned above[44,45,47] were only aimed at reproducing the levels in the HCN well and not in the CNH one.

Some tools, based on a matrix version of the Feshbach approach[54] or on the vibrationally adiabatic approximation,[55–61] have been developed for floppy systems and applied to the HCN/HNC and acetylene/vinylidene isomers. However, both methods are based on perturbation theory, not on *canonical* perturbation theory, and are not expected to be accurate enough for spectroscopic purposes in the field of highly excited vibrational states. On the other hand, CPT has been applied to mixed polynomial/trigonometric expansions in the treatment of torsions.[62–69] Yet, the purpose for doing so was principally to relate the experimentally accessible molecular parameters in the perturbative (or effective) Hamiltonian to the physically significant molecular parameters in the untransformed Hamiltonian in order to improve the fittings of the absorption frequencies of the studied molecules (almost exclusively methanol). The energy levels of the unperturbed Hamiltonian were neither calculated nor compared to those of the perturbative Hamiltonian, so that the actual accuracy of CPT remains unknown. Moreover, the barriers in the torsional problem are very low (of the order of 1 quantum of excitation in the torsional mode[70]) compared to the barriers in HCN or acetylene (several tens of quanta in the bending mode) and convergence properties might be expected to be more problematic in this latter case.

The purpose of the present article is to show that CPT might lead to very accurate perturbative Hamiltonians even for floppy molecules, provided that some changes are made in the procedures used up to now. Following the ''mixed diagonalization'' scheme introduced by Hernandez,[71] the modes are first sorted into two categories, which, in our procedure, can be described as oscillator-like ones (for example, the two stretching degrees of freedom in HCN/CNH) and hindered-rotor-like ones (for example, the bending in HCN/CNH). As in the usual procedure, the Hamiltonian is expanded as a polynome in terms of the oscillator-like modes, and the goal of CPT is to rewrite the Hamiltonian in terms of the action integrals and/or the good quantum numbers associated with these degrees of freedom. In contrast, much more general expressions are tolerated for hindered-rotor-like coordinates, but no classical constant of the motion or good quantum number is searched (nor is expected to exist) for these latter coordinates.

The remainder of this article is organized as follows: the procedure we suggest for applying CPT to floppy molecules is described in Sec. II. It is presented in the context of the Birkhoff–Gustavson perturbation theory, but extension to the other CPTs is straightforward. In Sec. III this scheme is shown to give excellent results for a two-dimensional model, which mimics the CH stretching and the bending degrees of freedom of nonlinear HCN. Finally, a more complex three-dimensional model, where the degeneracy of the bending motion of linear HCN is explicitly taken into account, is handled in Sec. IV and CPT is again shown to be very accurate.

II. DESCRIPTION OF THE PERTURBATION PROCEDURE

A. The ⟨common⟩ perturbative scheme

Assume that ε is an arbitrarily small parameter and that the Hamiltonian $H(\mathbf{p},\mathbf{q})$ of the system is partitioned, according to some choice discussed later in this section, in the form

$$E = H(\mathbf{p},\mathbf{q}) = \sum_n \varepsilon^n H_n(\mathbf{p},\mathbf{q}). \tag{2.1}$$

Assume further that a canonical transformation from the $(\mathbf{p},\mathbf{q})$ set of conjugate coordinates to a new $(\mathbf{P},\mathbf{Q})$ set is defined through the generating function $F(\mathbf{P},\mathbf{q})$, such that

$$F(\mathbf{P},\mathbf{q}) = \mathbf{Pq} + \varepsilon^s W(\mathbf{P},\mathbf{q}), \tag{2.2}$$

where s is an integer known as the order of the perturbation and W some function of $\mathbf{P}$ and $\mathbf{q}$. Last, assume that the resulting Hamiltonian $\Gamma(\mathbf{P},\mathbf{Q})$ is expressed in the same form as the initial Hamiltonian

$$E = \Gamma(\mathbf{P},\mathbf{Q}) = \sum_n \varepsilon^n \Gamma_n(\mathbf{P},\mathbf{Q}). \tag{2.3}$$

Then, a simple Taylor expansion[9–12] shows that for each value of n

$$\Gamma_n = H_n + \sum_{(i_1,i_2,\ldots,i_F)} \frac{1}{\Pi_k i_k!} \left\{ \frac{\partial^i H_{n-is}}{\Pi_k \partial P_k^{i_k}} \prod_{k=1}^{F} \left(\frac{\partial W}{\partial q_k} \right)^{i_k} \right.$$
$$\left. - \frac{\partial^i \Gamma_{n-is}}{\Pi_k \partial q_k^{i_k}} \prod_{k=1}^{F} \left(\frac{\partial W}{\partial P_k} \right)^{i_k} \right\}_{\substack{\mathbf{q}=\mathbf{Q} \\ \mathbf{p}=\mathbf{P}}}, \tag{2.4}$$

where F is the number of position coordinates, $(i_1,i_2,\ldots,i_F)$ is a set of F positive integers, i is defined as $i=i_1+i_2+\cdots+i_F$, and the sum in Eq. (2.4) runs for all those values of $(i_1,i_2,\ldots,i_F)$ such that $1 \leq i \leq n/s$. In particular, for each value of n smaller than s, there exists no such set $(i_1,i_2,\ldots,i_F)$, so that

$$\forall n < s, \ \Gamma_n = H_n. \tag{2.5}$$

Application of CPT consists of the iteration of the procedure outlined in Eqs. (2.1) through (2.4) for values of s increasing from $s=1$ up to some maximum value $s=S$. This means that the output function Γ obtained from Eq. (2.4) at the end of step s is used as the input function H in Eq. (2.1) at the beginning of step $s+1$. After iteration S is completed, the terms Γ_n with $n>S$, which are expected to be negligible, are dropped. The resulting perturbative Hamiltonian is then

$$H = \sum_{s=1}^{S} \Gamma_s. \tag{2.6}$$

The goal for applying CPT is to obtain a perturbative Hamiltonian in Eq. (2.6), which is both close to the initial one and much easier to handle. In the cases where CPT is successful, this is made possible by the fact that approximate constants of the motion (also called ''secular'' or ''almost secular'' terms) are hidden behind the apparent complexity of the initial Hamiltonian. The canonical transformations in Eqs. (2.2)

through (2.4) are precisely aimed at rewriting the Hamiltonian in terms of these constants of the motion.

It should then be clear that the key features in CPT are the initial partitioning into a sum of H_n's in Eq. (2.1) and the choice of the generating functions W in Eq. (2.2). Indeed, one has to make sure in the initial partitioning that H_0 contains only secular terms and, at each order $s \geqslant 1$, that the function W in Eq. (2.2) be chosen such that the resulting Γ_s obtained from Eq. (2.4) also contains only secular terms. The reason is, according to Eq. (2.5), that terms with $n < s$ are no longer modified by the perturbation calculations at order s, so that a bad choice for W and the appearance of nonsecular terms in a given Γ_s cannot be corrected at higher orders.

The general scheme described in Eqs. (2.1) through (2.6) is common to the standard Birkhoff–Gustavson perturbation theory[9–12] (BGPT) and the modified procedure we propose for the study of floppy molecules. The two methods, however, differ precisely in the expressions allowed for the initial Hamiltonian H, in the choice of the initial partitioning in Eq. (2.1) and of the secular terms to be kept in the perturbative Hamiltonian, and therefore in the generating function W in Eq. (2.2). The standard BGPT procedure is summarized in subsection B just below, in order to emphasize the differences with the modified procedure described in subsection C. For the sake of clarity, only the case where all the nonlinear resonances are negligible is treated, but the results extend readily to the cases where Fermi or other resonances must be taken into account.

B. The standard BGPT procedure

According to standard BGPT, both the potential and kinetic energies must consist of polynomial expansions around a minimum of the potential energy. Whenever necessary, Wilson's GF procedure[72] is applied, so that the lowest order (quadratic) terms are reduced to a sum of uncoupled harmonic oscillators. This sum is taken as H_0. Next, each term of the expansion of total degree n ($n \geqslant 3$) is arbitrarily put in H_{n-2}. Equation (2.4) shows that if W is always chosen as an homogeneous polynome of degree $s+2$ at order s of perturbation theory, then all the H_n and Γ_n remain homogeneous polynomes of degree $n+2$. The method[9–12] for finding the explicit expression for W at some given order s of BGPT first requires that H_s be rewritten in terms of a new set of coordinates, which are just the classical analogs of the quantum creation and annihilation operators, and which we therefore call $\mathbf{a}$ and $\mathbf{a}^+$

$$\mathbf{a} = \frac{1}{\sqrt{2}}(\mathbf{q} + i\mathbf{p}) \quad \mathbf{a}^+ = \frac{1}{\sqrt{2}}(\mathbf{q} - i\mathbf{p}). \tag{2.7}$$

One obtains

$$H_s = \sum_{\mathbf{m},\mathbf{l}} A_{\mathbf{m},\mathbf{l}} \left(\prod_{k=1}^{F} a_k^{m_k}(a_k^+)^{l_k} \right), \tag{2.8}$$

where the positive (or null) integers m_k and l_k satisfy $\Sigma_{k=1}^{F} m_k + l_k = s + 2$. If all the nonlinear resonances can be neglected, then the secular terms to be kept in Γ_s are those which satisfy $m_k = l_k$ (for $k = 1, 2, ..., F$). This is clearly understood when referring to the quantum picture, since they are

precisely the terms of the diagonal Dunham expansion. In order to obtain this result, one just needs to take W in the form

$$W(\mathbf{P}, \mathbf{q}) = \sum_{\mathbf{m} \neq \mathbf{l}} A_{\mathbf{m},\mathbf{l}} \frac{\Pi_{k=1}^{F}(q_k + iP_k)^{m_k}(q_k - iP_k)^{l_k}}{\Sigma_{k=1}^{F} i\omega_k(m_k - l_k)}, \tag{2.9}$$

where ω_k is the fundamental frequency of mode k, and $\mathbf{m} \neq \mathbf{l}$ means that at least one m_k is different from the associated l_k. At the end of the perturbation calculations, the resulting perturbative Hamiltonian in Eq. (2.6), therefore, is

$$H = \sum_{k} \omega_k I_k + \sum_{k \leqslant l} x_{kl} I_k I_l + \sum_{k \leqslant l \leqslant m} y_{klm} I_k I_l I_m + \cdots, \tag{2.10}$$

where I_k denotes the action integral of the kth harmonic oscillator

$$I_k = a_k a_k^+ = \tfrac{1}{2}(p_k^2 + q_k^2). \tag{2.11}$$

Stated in other terms, the perturbative Hamiltonian is just a polynomial expansion in terms of a complete set of constants of the motion I_k, the terms with total power n in the actions I_k being obtained at order $2n-2$ of perturbation theory.

C. The modified procedure

It is clear that the procedure described in the previous subsection cannot satisfactorily handle a PES with several equilibrium positions. The principal reason is that the motion is too different from one well to another to be described by a single oscillator. A prototypical example is the HCN/CNH molecule, for which there exist several global surfaces.[73–78] When moving along the minimum energy path (or reaction path), one observes two minima separated by a saddle point. The deepest minimum corresponds to the linear HCN isomer, whereas the second minimum, located roughly 5000 cm^{-1} above the first one, corresponds to the linear CNH isomer. The barrier to isomerization is found at an angle HCN of approximately 80° and an energy about 15 000 cm^{-1} above the HCN minimum. When considering the bending degree of freedom alone, the analogy with the problem of the hindered rotor is striking: motion in each well (i.e., below the saddle point) can be described as a libration, whereas motion above the saddle point corresponds to the rotational motion of the hindered rotor.

Accordingly, the principal idea at the basis of the modified procedure is to sort the degrees of freedom into two categories, namely oscillator-like ones [hereafter denoted $(\mathbf{p}, \mathbf{q})$] and hindered-rotor-like ones [hereafter denoted $(\mathbf{j}, \Psi)$—be careful, however, that the $(\mathbf{j}, \Psi)$ are vibrational coordinates, not rotational ones], and to apply CPT only to the former ones. To do so, one starts the perturbation procedure with a Hamiltonian in the form

$$E = H(\mathbf{p}, \mathbf{q}, \mathbf{j}, \Psi)$$

$$= \sum_{k=1}^{N} \frac{\omega_k}{2}(p_k^2 + q_k^2) + \sum_{\mathbf{u}, \mathbf{v}} \left(\prod_k p_k^{u_k} q_k^{v_k} \right) f_{\mathbf{u}, \mathbf{v}}(\mathbf{j}, \Psi), \tag{2.12}$$

where N is the number of oscillator-like coordinates and the $f_{\mathbf{u},\mathbf{v}}$ might be any function of the $(\mathbf{j},\Psi)$ hindered-rotor-like coordinates. For most systems (like the HCN/CNH or acetylene/vinylidene molecules) there exists a single hindered-rotor-like degree of freedom Ψ and Eq. (2.12) is simply arrived at by (i) expanding for each value of Ψ the Hamiltonian in Taylor series in terms of the deviations of the oscillator-like coordinates from their value at the reaction path, and (ii) Fourier transforming the result with respect to Ψ.

Let us now assume that H_s, at the beginning of the calculations at some order s of perturbation, is expressed in a form similar to Eq. (2.8), plus some general dependence in $(\mathbf{j},\Psi)$

$$H_s = \sum_{\mathbf{m},\mathbf{l}} A_{\mathbf{m},\mathbf{l}} g_{\mathbf{m},\mathbf{l}}(\mathbf{j},\Psi) \left(\prod_{k=1}^{N} a_k^{m_k} (a_k^+)^{l_k} \right). \qquad (2.13)$$

The $g_{\mathbf{m},\mathbf{l}}$ are known functions of the $(\mathbf{j},\Psi)$ hindered-rotor-like coordinates, but the condition $\Sigma_{k=1}^{N} m_k + l_k = s+2$ is no longer required, in contrast with subsection B. If the nonlinear resonances are negligible, the terms to be kept in the perturbative Hamiltonian (i.e., in Γ_s) are again those with $m_k = l_k$ (for $k = 1,2,...,N$). Indeed, these terms depend only on the hindered-rotor-like coordinates and the action integrals associated with the N oscillator-like degrees of freedom. Straightforward calculations show that this might be obtained with a generating function W transforming $(\mathbf{p},\mathbf{q})$ and $(\mathbf{j},\Psi)$ into $(\mathbf{P},\mathbf{Q})$ and $(\mathbf{J},\psi)$ rather similar to the standard BGPT procedure in Eq. (2.9), that is

$$W(\mathbf{P},\mathbf{J},\mathbf{q},\Psi) = \sum_{\mathbf{m}\neq\mathbf{l}} A_{\mathbf{m},\mathbf{l}} g_{\mathbf{m},\mathbf{l}}(\mathbf{J},\Psi)$$

$$\times \frac{\Pi_{k=1}^{N}(q_k + iP_k)^{m_k}(q_k - iP_k)^{l_k}}{\Sigma_{k=1}^{N} i\omega_k(m_k - l_k)}, \quad (2.14)$$

provided, however, that the initial choice for H_0 does not depend on the hindered-rotor-like coordinates. This condition is absolutely crucial : if it is not fulfilled, then Eq. (2.4) (where $P_{N+1},...,P_F$ must obviously be understood as $J_1,...,J_{F-N}$, $q_{N+1},...,q_F$ as $\Psi_1,...,\Psi_{F-N}$, and so on) shows that a large number of spurious terms are left in Γ_s at each order s of perturbation theory. Therefore, the natural choice consists in taking H_0 as the sum of the N uncoupled harmonic oscillators associated with the oscillator-like degrees of freedom, that is, the first term in the right-hand side of Eq. (2.12). One might feel uncomfortable that the zero-order Hamiltonian contains strictly no information concerning the hindered-rotor-like degrees of freedom, but the numerical examples in the next sections show that this is actually of no consequence. The choice for the partitioning into higher-order terms H_n $(n \geqslant 1)$ might appear to be tricky, because one does not know how to handle the functions $f_{\mathbf{u},\mathbf{v}}(\mathbf{j},\Psi)$ as far as some ordering is required (the ordering proposed in the framework of the torsional problem[62–69] will be shown in the next section to be a bad choice for the present problem). Here, it must however be stressed that such an ordering into increasing H_n's $(n \geqslant 1)$ is *not* compulsory, but is instead only aimed at simplifying somewhat the

calculations. For example, the choice that the initial H_n's $(n \geqslant 1)$ be homogeneous polynomes of degree $n+2$ in standard BGPT insures that all the H_n and the W remain homogeneous polynomes, whatever the order s of the perturbation, and consequently that each term

$$\prod_{k=1}^{F} I_k^{m_k}$$

appears only once in the perturbation scheme, namely at order $2(m_1 + m_2 + \cdots + m_F) - 2$. It is therefore simply suggested that in the modified procedure *the sum of the N harmonic oscillators be put in H_0 and all the remaining terms, that is, the second term in the right-hand side of Eq. (2.12), in H_1* . The price to pay is a slightly higher number of terms to handle, which is not a serious drawback—and this procedure is much less dangerous than tempting some hazardous ordering. One must also be aware that the same term might appear at different orders of perturbation theory (that is, in various Γ_s): these contributions just have to be summed up at the end of the perturbative scheme, leading to a perturbative Hamiltonian of the form

$$H = E_0(\mathbf{j},\Psi) + \sum_{k} \omega_k(\mathbf{j},\Psi) I_k + \sum_{k \leqslant l} x_{kl}(\mathbf{j},\Psi) I_k I_l$$

$$+ \sum_{k \leqslant l \leqslant m} y_{klm}(\mathbf{j},\Psi) I_k I_l I_m + \cdots . \qquad (2.15)$$

This expression is a polynome in terms of the N constants of the motion I_k associated with the oscillator-like degrees of freedom, whereas the dependence on the F–N hindered-rotor-like degrees of freedom might be much more complex. Stated in other terms, one constant of the motion is lost for each hindered-rotor-like degree of freedom. It is to be noted that the loss of one simple constant of motion is also the price to pay for taking into account one nonlinear resonance between the zero-order normal modes, even in the usual case of a PES with a single equilibrium position. This similarity is due to the fact that both a saddle point and a nonlinear resonance might lead to bifurcations, that is, to discontinuities in the phase space structure and the zero-order description of the system.

For the sake of illustration, the modified procedure is applied in the next section to a 2D model, which mimics the CH stretching and the bending degrees of freedom of nonlinear HCN, and in Sec. III to a more complex 3D model where the degeneracy of the bending motion of linear HCN is explicitly taken into account.

III. APPLICATION TO A TWO-DIMENSIONAL MODEL FOR NONLINEAR HCN

The model Hamiltonian is taken to be

$$H = T + V,$$

$$\hbar^2 T = A p_R^2 + B p_\gamma^2,$$

$$V = V_1 \cos \gamma + V_2 \cos 2\gamma + (f_{RR} + f_{RR\gamma\gamma} \cos \gamma)$$

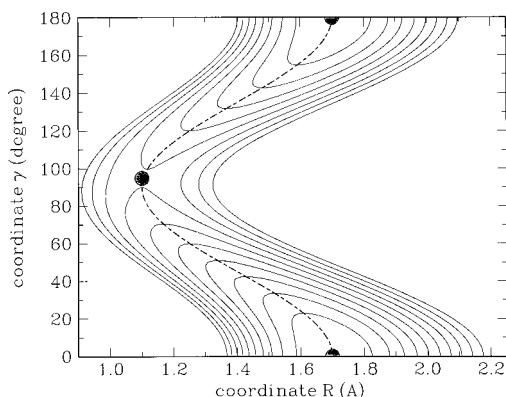$$\times (R - \alpha - \beta \cos 2\gamma)^2 + f_{RRR}(R - \alpha - \beta \cos 2\gamma)^3, \qquad (3.1)$$

FIG. 1. Contour plot of the potential energy V in Eq. (3.1). The contours (solid lines) are separated by 2000 cm^{-1} and range from 2000 to 20 000 cm^{-1} above the absolute minimum at $R=1.7$ Å and $\gamma=0$. The two other extrema found at $R=1.7$ Å and $\gamma=180°$ (secondary minimum) and $R=1.10$ Å and $\gamma=94.8°$ (saddle) are located, respectively, at 4000 and 14 083 cm^{-1} above the absolute minimum. The position of each extremum is marked with a black dot. The dashed line indicates the minimum energy path (MEP) linking the three of them [see Eq. (3.2)].

where (p_R,R) and (p_γ,γ) are two sets of conjugate coordinates, which mimic, respectively, the distance between H and the center of mass G of CN and the HGC angle in HCN (R and γ are so-called Jacobi coordinates). The very simple form of T in Eq. (3.1) is assumed in order for full quantum mechanical calculations to remain affordable to us (see below). Numerical values for A and B are taken to be $A=17.6$ cm^{-1}Å^2 and $B=6.0$ cm^{-1}. On the other hand, V in Eq. (3.1) is one of the simplest surfaces displaying two wells centered around $\gamma=0$ and $\gamma=\pi$ and connected by a curved reaction path (or minimum energy path: MEP). Here, the MEP is simply characterized by

$$R_{\mathrm{MEP}}(\gamma)=\alpha+\beta\cos 2\gamma, \qquad (3.2)$$

but in more general cases, its characterization requires that the value of each oscillator-like coordinate along the reaction path be expanded in a complete Fourier series in terms of the hindered-rotor-like coordinate. The values $\alpha=1.4$ Å, $\beta=0.3$ Å, $V_1=-2000$ cm^{-1}, and $V_2=-6000$ cm^{-1} are chosen so as to reproduce, at least qualitatively, the principal features of HCN: in particular, the saddle point and the secondary minimum are calculated at 14 083 and 4000 cm^{-1} above the absolute minimum, respectively. Moreover, the values of the force constants for the stretching degree of freedom ($f_{RR}=145\,000$ cm^{-1}Å^{-2} and $f_{RRR}=-115\,000$ cm^{-1}Å^{-3}) and for the stretch–bend interaction ($f_{RR\gamma\gamma}=-1800$ cm^{-1}Å^{-2}) are chosen so as to lead to realistic parameters ω, k, and λ (see below). A contour plot of the surface V is given in Fig. 1 and is seen to compare well with similar figures for HCN, for example, Fig. 4 of Ref. 77.

Application of the canonical transformation to the new sets of conjugate coordinates (p,q) and (j,Ψ), according to

$$q=\rho(R-R_{\mathrm{MEP}}(\gamma)), \quad p_R=\rho p$$
$$\qquad (3.3)$$
$$\Psi=\gamma, \quad p_\gamma=j-\rho\frac{\partial R_{\mathrm{MEP}}}{\partial\gamma}p,$$

where $\rho=(f_{RR}/(A+2\beta^2B))^{1/4}$, leads to the following expression for the Hamiltonian:

$$\hbar^2T=\frac{\omega}{2}p^2+Bj^2+C\sin(2\Psi)jp+D\cos(4\Psi)p^2,$$
$$\qquad (3.4)$$
$$V=\frac{\omega}{2}q^2+kq^3+V_1\cos\Psi+V_2\cos 2\Psi+\lambda q^2\cos\Psi,$$

with:

$$\omega=2f_{RR}\rho^{-2}\approx 3291.56 \text{ cm}^{-1},$$
$$C=4\beta B\rho\approx 67.58 \text{ cm}^{-1},$$
$$k=f_{RRR}\rho^{-3}\approx -139.06 \text{ cm}^{-1}, \qquad (3.5)$$
$$D=-2\beta^2B\rho^2\approx -95.15 \text{ cm}^{-1}.$$
$$\lambda=f_{RR\gamma\gamma}\rho^{-2}\approx -20.43 \text{ cm}^{-1},$$

The couplings between the two modes (terms with C, D, and λ) are seen to be strong. Using the convention that $\hbar=1$, H is next partitioned into H_0+H_1, where:

$$H_0=\frac{\omega}{2}(p^2+q^2),$$
$$\qquad (3.6)$$
$$H_1=kq^3+V_1\cos\Psi+V_2\cos 2\Psi+\lambda q^2\cos\Psi+Bj^2$$
$$\qquad +C\sin(2\Psi)jp+D\cos(4\Psi)p^2.$$

The modified CPT procedure described in the previous section is then applied to the Hamiltonian in Eq. (3.6). The general result of Eq. (2.15) is obtained here in the form

$$H=\sum_{k,m,n}a_{k,m,n}I^kj^m\cos(n\Psi). \qquad (3.7)$$

Although a cutoff value of 10^{-10} cm^{-1} was used in actual calculations, there are too many coefficients $a_{k,m,n}$ to present an exhaustive table thereof. Still, Table I gives a flavor of how some parameters evolve with increasing perturbation order. As could be expected, the general trend is that the contribution to each parameter decreases as the perturbation order increases (note, however, that a correction of 15.61 cm^{-1} to the fundamental frequency $a_{1,0,0}$ is calculated at third order of perturbation theory).

The remainder of this section is devoted to a discussion of the accuracy of the perturbative Hamiltonian in Eq. (3.7). A straightforward method for comparing two Hamiltonians, which are not expressed in terms of the same coordinates, consists in comparing the spectra of their quantum analogs. This is admittedly not a trivial problem from the theoretical point of view, even for the simple polynomial expressions obtained from usual BGPT,[41,79–81] because conjugate position and momentum operators do not commute. From the practical point of view, however, it is noted that the various ordering possibilities lead to very close spectra[52] (a more detailed discussion of this point will be presented somewhat later in this section). The results presented below have been obtained by quantizing each classical term $j^m\cos(n\Psi)$ according to Weyl's rule

TABLE I. Contributions (in cm^{-1}) to the coefficients of the terms in I, I^2, j^2, j^4, cos Ψ, cos 2Ψ, and cos 4Ψ in the expression of the perturbative Hamiltonian H in Eq. (3.7) calculated for increasing perturbation order s. The total coefficients of the Hamiltonian H in Eq. (3.7) at a given order s are obtained by summing all the contributions from 0 up to s. For example, the fundamental frequency $a_{1,0,0}$ (coefficient of the term I) at perturbation order $s=3$ is calculated to be $a_{1,0,0}=3291.5600+0.0000-0.7193+15.6131=3306.4538$ cm^{-1}.

Coefficient→ Term→ Order s ↓	$a_{1,0,0}$ I	$a_{2,0,0}$ I^2	$a_{0,2,0}$ j^2	$10^5 \times a_{0,4,0}$ j^4	$a_{0,0,1}$ cos Ψ	$a_{0,0,2}$ cos 2Ψ	$a_{0,0,4}$ cos 4Ψ
0	3291.5600	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.0000	0.0000	6.0000	0.0000	−2000.0000	−6000.0000	0.0000
2	−0.7193	−22.0310	−0.3469	0.0000	0.0000	0.0000	0.0000
3	15.6131	0.0251	0.0100	0.0000	0.0000	0.0000	0.0000
4	0.2461	−0.0011	−0.0006	−1.8441	−1.1526	0.0320	4.6744
5	0.0649	0.3999	0.0000	0.1066	0.0454	0.0000	−0.4644
6	−0.1789	0.0088	−0.0010	−0.0279	−0.0010	0.0000	0.0172
7	0.0042	0.0048	0.0001	0.0114	0.0096	0.0088	−0.0300
8	−0.0037	−0.0125	0.0000	−0.0457	−0.0044	0.0000	0.0060

$$j^m \cos(n\Psi) \rightarrow \frac{1}{2^m} \sum_{k=0}^{m} \binom{m}{k} (j^k \cos(n\Psi) j^{m-k}). \qquad (3.8)$$

The spectrum for the exact Hamiltonian in Eq. (3.4) was obtained by direct diagonalization of a 1654*1654 matrix, each vector of the basis $|v\rangle \otimes |m\rangle$ being the direct product of a vector of the harmonic oscillator basis ($0 \leq v \leq 16$) and of the free rotor basis ($-101 \leq m \leq 101$). The harmonic oscillator basis is obviously used for the p and q operators and the free rotor basis for the j and Ψ operators. The first 158 levels up to 15 000 cm^{-1} above the ground state are estimated to be converged to within less than 0.2 cm^{-1}. Each state was assigned two quantum numbers (v_s, v_b) and a localization flag (localized in the $\gamma=0$ well, localized in the $\gamma=\pi$ well, or delocalized) through inspection of the wave functions. One hundred thirty-six out of these 158 levels are localized into one of the wells, while the remaining 12 levels are delocalized over the two wells. These 12 levels have no excitation in the stretching degree of freedom ($v_s=0$). In contrast, the stretching quantum number v_s, which is the quantum counterpart of the classical action integral I, is by construction a conserved quantity for the perturbative Hamiltonian in Eq.

(3.7). Therefore, one only needs to diagonalize six much smaller matrices of size 121*121 ($-60 \leq m \leq 60$), one for each value of $v_s=0,1,...,5$, in order for the same 158 levels to be converged to within less than 0.001 cm^{-1}. Assignment of the spectrum is also much simpler.

The average absolute difference between the two assigned spectra is presented in Table II for increasing perturbation order s. More precisely, the error for the first 100 states is given for s ranging from 1 to 8, whereas the error for the first 158 states is given only for values of s larger than 4, because for lower values the distribution into localized/delocalized states is not the same for the exact and perturbative Hamiltonians. It is seen that the convergence is excellent, the error for the first 158 states being as low as 1.99 cm^{-1} at fourth order of perturbation theory. The error at eighth order of perturbation theory is further plotted in Fig. 2. It is seen that the largest errors occur in pairs of opposite values. For example, levels #76 and #77 are calculated with respective errors of −12.5 and +12.1 cm^{-1}, levels #137 and #139 with respective errors of −10.1 and +9.2 cm^{-1}, and so on. Looking at the assignments, one notices that these levels are, respectively, described as (v_s, v_b)=(0,23) and (1,15) (well around $\gamma=0$) for the first pair of states, (v_s, v_b) =(2,15) and (1,23) (well around $\gamma=0$) for the second one,

TABLE II. Difference between the assigned spectra of the exact Hamiltonian in Eq. (3.4) and the perturbative Hamiltonian in Eq. (3.7) for increasing order s of perturbation theory. Columns 2 and 3 give, respectively, the average absolute and maximum errors for the first 100 levels and columns 4 and 5 the average absolute and maximum errors for the first 158 levels. The blanks in these later columns for $s=1$ to $s=3$ are due to the fact that for these lowest values of s the number of localized and delocalized states is not the same for the exact and perturbative Hamiltonians.

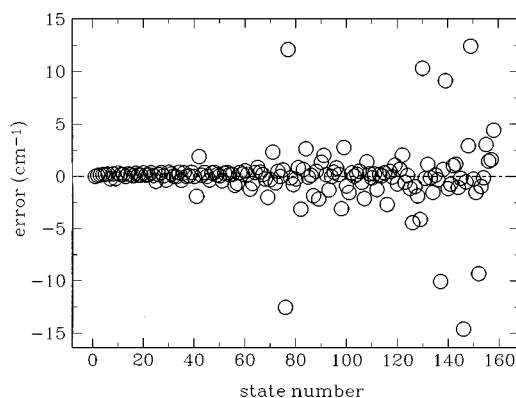| Order s	100 levels		158 levels	
	Average	Max	Average	Max
1	146.35	318.64		
2	4.91	25.25		
3	10.90	40.03		
4	1.36	15.37	1.99	15.37
5	1.72	17.23	2.72	19.91
6	0.83	12.79	1.34	14.37
7	0.86	13.81	1.42	16.46
8	0.79	12.54	1.27	14.60

FIG. 2. Plot of the errors (in cm^{-1}) between exact and perturbative (eighth order) energy values as a function of the position of the level in the spectrum for the model Hamiltonian discussed in Sec. III.

TABLE III. Difference between the exact and perturbative energy values of some selected bending states $(0, v_b)$ as a function of the perturbation order s for the nondegenerate model of Sec. III. The second column indicates whether the state is localized in the $\gamma=0$ or in the $\gamma=\pi$ well. The third column contains the exact quantum energy of the state in cm^{-1} relative to the ground level. The errors in the last eight columns are expressed in cm^{-1}. The sudden increase of the error observed at third order of perturbation theory is probably connected to the large correction computed at the same order for the fundamental frequency $a_{1,0,0}$ (see Table I).

v_b	γ	Energy	$s=1$	$s=2$	$s=3$	$s=4$	$s=5$	$s=6$	$s=7$	$s=8$
1	0	558.66	1.91	−0.56	0.11	−0.13	−0.05	−0.09	−0.08	−0.08
15	0	7 502.63	198.26	8.32	18.10	1.52	2.53	0.11	0.56	0.01
30	0	13 124.35	291.15	14.35	28.55	2.95	5.15	−0.15	1.25	−0.45
1	π	4 511.49	2.01	−0.86	−0.05	−0.26	−0.20	−0.23	−0.22	−0.23
11	π	9 126.38	118.56	2.55	8.48	−0.05	0.60	−0.40	−0.19	−0.37
22	π	13 077.16	213.44	4.14	14.64	0.54	1.84	0.36	0.24	−0.36

and so on. The conclusion, which is confirmed by the examination of the wave functions, is therefore that the largest errors observed in Fig. 2 are due to the weak 1:8 (and also 1:6) resonances between the two modes, which become locally noticeable in the exact quantum spectrum in the case of accidental near degeneracy of the uncoupled levels. Calculations show that, for $s\geq 6$, the five pairs of most strongly coupled levels are responsible for 50% of the average difference between the first 100 levels of the exact and perturbative spectra. The origin of the remaining 0.4 cm^{-1} average error is less clear. It is probably due in part to the accidental resonances discussed just above (but for levels further from degeneracy) and in part to the quantization rule in Eq. (3.8). Indeed, use of a simpler quantization rule, according to

$$j^m \cos(n\Psi) \rightarrow \tfrac{1}{2}(j^m \cos(n\Psi) + \cos(n\Psi)j^m), \qquad (3.9)$$

leads, at eighth order of perturbation, to levels which differ on average by 0.43 cm^{-1} and at maximum by 1.22 cm^{-1} from the 158 perturbative levels obtained using Eq. (3.8). Since the use of two different quantization rules leads to a difference of several tenths of a cm^{-1}, it cannot be excluded that part of the remaining 0.4 cm^{-1} error between the exact and perturbative spectra is due to the use of the approximate Weyl quantization rule in Eq. (3.8). A full quantum version of the procedure described in Sec. II would be needed to check this point. Anyway, the residual resonances and eventually the approximate quantization scheme are responsible for the fact that increasing s from 6 up to 8 does not improve the convergence further.

A complementary insight into the convergence properties of the modified CPT procedure is provided by the examination of the errors for some specific bending states $(0, v_b)$ reported in Table III. Errors for s increasing from 1 to 8 are shown for the states with $v_b = 1$, 15, and 30 in the well centered around $\gamma=0$ and $v_b = 1$, 11 and 22 in the well centered around $\gamma=\pi$. The main information is that the convergence properties and the relative errors (that is, the errors divided by v_b) are of the same order of magnitude for all these levels. This uniformity differs markedly from usual procedures, for which low-lying levels converge much more rapidly (i.e., at much lower order s) than highly excited ones. The most probable reason is that all the terms, except for the harmonic oscillators, are put in H_1 in the procedure described in Sec. II, whereas terms with increasing powers, which become important for highly excited states, are ini-

tially put in higher terms H_n in the usual procedure and are therefore first taken into account at correspondingly higher orders of perturbation theory.

Before concluding this section, it is worth noting that for the simple model in Eq. (3.1) the procedure proposed in Sec. II happens to be close to that used in the torsional problem,[62–69] the major difference arising precisely from the initial ordering of the terms into the H_n. Indeed, according to the prescriptions in Refs. 62–69, the terms kq^3, bj^2, and $V_1(1-\cos\Psi)$ should be put in H_1, $V_2(1-\cos 2\Psi)$, and $\lambda q^2(1-\cos\Psi)$ in H_3, $Cjp(\sin 2\Psi)$ in H_5, and $Dp^2(1-\cos 4\Psi)$ in H_9. Since the terms with C and D are so important, this ordering scheme clearly cannot work in the present case. Calculations effectively show that the average error at 12th order with the torsional ordering scheme is still about one order of magnitude larger than the error observed at sixth order with the ordering scheme in Sec. II (10.23 cm^{-1} vs 1.34 cm^{-1}).

IV. APPLICATION TO A THREE-DIMENSIONAL MODEL FOR LINEAR HCN

The same model as in Sec. III, but with a degenerate bending vibration instead of a nondegenerate one, is written in the form

$$H = T + V,$$

$$\hbar^2 T = A p_R^2 + B\left(p_\gamma^2 + \frac{p_\chi^2}{\sin^2\gamma}\right), \qquad (4.1)$$

$$V = V_1 \cos\gamma + V_2 \cos 2\gamma + (f_{RR} + f_{RR\gamma\gamma}\cos\gamma)$$
$$\times (R - \alpha - \beta\cos 2\gamma)^2 + f_{RRR}(R - \alpha - \beta\cos 2\gamma)^3,$$

where χ is the rotation angle around the axis of inertia with smallest momentum and p_χ is the momentum conjugate to χ. The kinetic energy in Eq. (4.1) is seen to display the usual singularity for the linear configurations at $\gamma=0$ and $\gamma=\pi$. Using the canonical transformation in Eq. (3.3), the Hamiltonian is rewritten in the form

$$\hbar^2 T = \frac{\omega}{2} p^2 + B\left(j^2 + \frac{p_\chi^2}{\sin^2\Psi}\right) + C \sin(2\Psi) jp$$
$$+ D \cos(4\Psi) p^2, \qquad (4.2)$$

$$V = \frac{\omega}{2} q^2 + k q^3 + V_1 \cos \Psi + V_2 \cos 2\Psi + \lambda q^2 \cos \Psi,$$

where ω, k, λ, C, and D are the same as in Eq. (3.5). The basis adapted to the Hamiltonian in Eq. (4.2) consists of direct products of the form $|v\rangle \otimes |m,l\rangle$, where $|v\rangle$ is a vector of the harmonic oscillator basis and $|m,l\rangle$ denotes the spherical harmonic $Y_m^l(\Psi,\chi)$. Use of this basis solves the problem of the singularity at linear configurations, since

$$\left(j^2 + \frac{p_\chi^2}{\sin^2 \Psi} \right) |m,l\rangle = m(m+1)|m,l\rangle$$

$$p_\chi |m,l\rangle = l|m,l\rangle. \tag{4.3}$$

The vibrational angular momentum l is a good quantum number for the Hamiltonian in Eq. (4.2). For each value of l, the spectrum is obtained by direct diagonalization of a matrix of size up to $1382*1382$ for $l=0$ ($0 \leqslant v \leqslant 20$ and $l \leqslant m \leqslant 131$). All the levels up to $15\,000$ cm^{-1} above the ground state are estimated to be converged to within less than 0.01 cm^{-1}. As for the nondegenerate case in Sec. III, each state is further assigned a stretching quantum number v_s, a bending quantum number v_b, and a localization flag (localized around $\gamma=0$ or $\Psi=\pi$, or delocalized) through inspection of its wave functions.

As far as quantum results are needed for the perturbative Hamiltonian, it is not wise to apply CPT directly to the expression in Eq. (4.2). Indeed, this leads to complex operators involving inverse and powers of trigonometric functions, for which no matrix representation can be found. In contrast, every function of $j^2 + p_\chi^2/\sin^2 \Psi$ and p_χ, no matter how complex, has a trivial matrix representation because these operators are diagonal in the $|m,l\rangle$ basis [see Eq. (4.3)]. Therefore, it is better to perform an additional canonical transformation before applying CPT. The function

$$F(M,L,\Psi,\chi) = M \left(\frac{\pi}{2} - \arcsin \frac{M \cos \Psi}{\sqrt{M^2 - L^2}} \right)$$

$$+ L \left(\chi + \arctan \frac{L \cos \Psi}{\sqrt{M^2 \sin^2 \Psi - L^2}} \right), \tag{4.4}$$

generates a canonical transformation from (j,Ψ) and (χ, p_χ) to (M,θ) and (L,φ), such that

$$j^2 + \frac{p_\chi^2}{\sin^2 \Psi} = M^2, \quad \cos \Psi = \sqrt{1 - \frac{L^2}{M^2}} \cos \theta$$

$$p_\chi = L, \quad j \sin 2\Psi = \left(1 - \frac{L^2}{M^2} \right) M \sin 2\theta. \tag{4.5}$$

Upon expression of the Hamiltonian in Eq. (4.2) in terms of these new coordinates and application of the modified CPT procedure of Sec. II, the general result of Eq. (2.15) is obtained in the form

$$H = \sum_{k,m,p,q,n} b_{k,m,p,q,n} I^k M^p L^m \left(1 - \frac{L^2}{M^2} \right)^q \cos(n\theta), \tag{4.6}$$

where the indices k, m, and n are positive, p can be positive or negative, and q is either half-integral (positive or nega-

TABLE IV. Exact and perturbative (third order) values for the energy splitting Δ_{0-l} between the states (v_b, l) and $(v_b, 0)$ for some selected bending states ($v_s = 0$) in both wells. The value of v_b is given in the first column. The second column indicates whether the state is localized in the $\gamma=0$ or in the $\gamma=\pi$ well. The third column contains the exact quantum energy of the state with $l=0$ in cm^{-1} relative to the ground level. The next four columns contain the exact and perturbative values of the splittings Δ_{0-l} (in cm^{-1}) for $l=2$, 4, 6, and 8.

		Energy	Δ_{0-2}		Δ_{0-4}		Δ_{0-6}		Δ_{0-8}	
v_b	γ	$(l$-$0)$	Exact	CPT	Exact	CPT	Exact	CPT	Exact	CPT
2	0	1 098.8	18.3	18.9						
10	0	5 157.9	17.2	18.1	68.8	65.0	154.5	137.7	274.0	249.6
18	0	8 720.1	16.8	13.2	67.1	60.0	150.8	134.4	267.6	228.5
26	0	11 745.3	17.1	13.2	68.6	53.8	154.2	126.6	273.6	236.3
2	π	3 975.4	18.8	19.4						
8	π	7 777.6	17.9	18.7	71.4	66.5	160.4	147.6	284.4	274.3
14	π	10 245.1	17.5	14.8	70.1	62.6	157.5	134.7	279.5	236.5
20	π	12 346.0	17.9	13.6	71.5	57.0	160.7	133.0	285.0	235.6

tive) or zero. This expression differs markedly from the results of the torsional problem; related calculations consume substantially more computer time and memory. For quantum calculation purposes, the result in Eq. (4.6) is expressed back in the (j,Ψ) and (χ, p_χ) sets of coordinates and quantized according to

$$\left(j^2 + \frac{p_\chi^2}{\sin^2 \Psi} \right)^{p/2} \left(1 - \frac{p_\chi^2}{j^2 + \frac{p_\chi^2}{\sin^2 \Psi}} \right)^q \cos(n\Psi)$$

$$\rightarrow \frac{1}{2} \left(\left(j^2 + \frac{p_\chi^2}{\sin^2 \Psi} \right)^{p/2} \right.$$

$$\times \left(1 - \frac{p_\chi^2}{j^2 + \frac{p_\chi^2}{\sin^2 \Psi}} \right)^q \cos(n\Psi) + \text{h.c.} \left. \right), \tag{4.7}$$

where h.c. means the hermitian conjugate of the preceding expression. The Hamiltonian matrix is then built in the same basis of $|v\rangle \otimes |m,l\rangle$ vectors as the exact Hamiltonian. Diagonalization of a $71*71$ matrix for each value of v_s and l leads to levels which are converged to within less than 10^{-6} cm^{-1}. At second order of perturbation theory, the perturbative Hamiltonian in Eq. (4.6) is as accurate as the nondegenerate case for l smaller than 3 (about 5.9 cm^{-1} average error for all the levels up to $15\,000$ cm^{-1} above the ground state). The average error then increases rapidly, reaching 10.8 cm^{-1} for $l=4$, 22.6 cm^{-1} for $l=6$, and 38.5 cm^{-1} for $l=8$. At third order of perturbation theory, the accuracy is the same as for the nondegenerate case up to a higher value of $l=6$ and then worsens again rapidly for higher values of l. It seems to be a general property that the higher the vibrational angular momentum l, the higher the needed order of the perturbation theory for the corresponding subspectrum to be as accurate as the nondegenerate case or the subspectrum with $l=0$. Examination of Table IV, which displays the values of the energy splittings Δ_{0-l} between (v_b, l) and $(v_b, 0)$ for selected bending states ($v_s = 0$) with v_b up to 26 and selected values

of l ($0 \leqslant l \leqslant 8$) at third order of perturbation theory, further shows that this splitting is better reproduced for the smallest values of v_b. Last, it should be noted that the simpler computer code for the nondegenerate model in Sec. III can be used for the more complex degenerate model in Sec. IV, as long as only rotationless levels ($l = 0$) are needed. After the coefficients a or b have been computed, one must however be careful to use the correct basis set (if quantum calculations are performed) or the good Maslov indexes (if semiclassical quantization is used).

V. CONCLUSION

We have shown that CPT might be as accurate for floppy molecules as it was known to be for rigid ones. We now plan to apply the procedure described in Sec. II to more realistic surfaces, like those for HCN/CNH or acetylene/vinylidene, in order to see what can be learned concerning the highly excited vibrational dynamics of these molecules.

ACKNOWLEDGMENTS

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