

Computation of Nonlinear Optical Properties of Molecules with Large Amplitude Anharmonic Motions. III. Arbitrary Double-Well Potentials

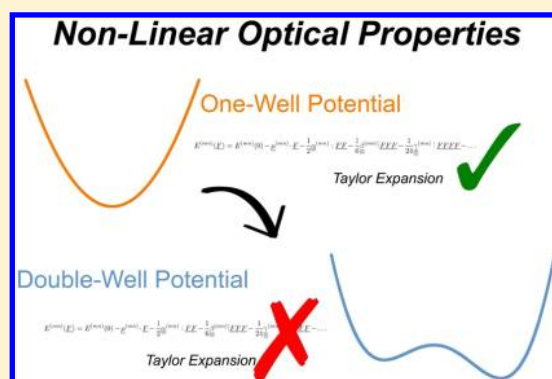
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ABSTRACT: Previously, a treatment of the vibrational contribution to nonlinear optical properties for molecules with large amplitude modes in a symmetric double-minimum potential well was devised. The vibronic energies were written as a power series in the field for two limiting cases of the ratio between the field-induced energy and the zero-field splitting energy of the two lowest vibronic states. This treatment is extended here to include all values of the ratio and also an asymmetric double-well potential. It is shown that a consistent treatment of NLO effects in the general case leads to new field expansion coefficients, which are formulated in terms of the usual dipole moment and (hyper)polarizabilities. As an example, the new treatment is applied to the inversion motion of CH_3^- .



1. INTRODUCTION

The importance of vibrational contributions to molecular linear and nonlinear optical properties is, by now, well recognized.^{1–12} On the other hand, their calculation can pose difficulties in particular cases and computational methods to deal with such instances effectively are still under active development. A perturbation treatment, based on a double harmonic initial approximation, was developed by Bishop and Kirtman (BKPT) a while ago^{13–15} and is still actively employed. Due to its perturbative character, however, BKPT cannot handle molecules with potential energy functions where several equivalent, or nearly equivalent, minima are separated by sufficiently low barriers, so that tunneling is important,¹⁶ which is the first paper in this series. A typical example is the umbrella mode in certain pyramidal AX_3 molecules. For such molecules, a new method based on an extension of the variational finite-field nuclear relaxation (FF-NR) treatment^{17,18} was recently presented, in which the umbrella mode is treated exactly by solving a reduced one-dimensional (1D) Schrödinger equation within the framework of Generalized Van Vleck perturbation theory. In FF-NR, the electronic electric dipole properties are computed at the (static) field-dependent optimized geometry and each property is, then, expanded as a power series in the field. The coefficients in these expansions are the sum of vibrational and electronic (hyper)polarizabilities, which may be either static or dynamic (in the so-called infinite optical frequency approximation), depending on the property used for the expansion.^{17–20} In a subsequent paper²¹ (paper II

of this series), the limitation of the 1D treatment was recognized and full dimensionality models were explored. The models used separate the vibrational coordinates into an active (1D or 2D) and an inactive set. For one or two active coordinates, the full vibrational potential is used, whereas the remaining modes are taken into account in a harmonic approximation.²¹ This was shown to be important to avoid spurious conclusions based on the simple 1D procedure.

In both previous papers, an additional limitation was introduced. It turned out that it is possible to write the energy as a power series in the field, only if the quantity $|\underline{\mu} \cdot \underline{E}|$, where $\underline{\mu}$ is the dipole moment and \underline{E} the electric field, is either much larger or much smaller than the inversion splitting of the vibrational ground state. Since the inversion splitting increases with decreasing potential barrier between the two wells, the first of these two limiting cases requires large fields in combination with medium barriers (high barriers lead to negligible tunneling and, thus, allow a treatment based on two separate wells), while the second case applies to low fields and low barriers. For all field strengths that could be applied in the calculations, the umbrella motion in NH_3 was found to fall into the high field/medium barrier category. No other molecules have been considered as yet. In particular, this leaves a gap for double-well potentials that do not fulfill either of the two limiting conditions. Examples for which this may be so can be found

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among pyramidal AX_3 systems with a double-well barrier considerably smaller than that of NH_3 , such as the methyl anion CH_3^- ,²² or the hydroxonium ion H_3O^+ .^{23,24}

Our preliminary attempts to determine the vibrational NLO properties of CH_3^- in either of the two limiting cases mentioned above did, indeed, prove unsuccessful. It is the purpose of this paper to generalize our approach so that such systems can also be treated. As we will show, the field-dependent energies for the two states of the lowest inversion doublet can be combined in such a way as to yield a pair of power series expansions in the field. Although not all of the coefficients can be interpreted as a dipole moment or a (hyper)polarizability in the usual sense, they turn out to be well-defined functions of the latter properties, as well as the inversion splitting. This new procedure is applied both to NH_3 , in order to show that it is consistent with our previous work, and to the CH_3^- anion, for which it is the only available treatment at present. In order to broaden the applicability of our new treatment, the formalism for two inequivalent wells with small asymmetry is also given.

2. THEORY

2.1. Asymmetric Double-Well Potential. We will consider a double-well potential with a small asymmetry. The meaning of ‘small’ will be clarified in the following. If the two wells are equivalent, then the lowest two states will be degenerate in the absence of tunneling. With tunneling switched on, these states will mix and the degeneracy (if initially present) will be lifted. For equivalent wells, the mixture will be symmetric and antisymmetric combinations with respect to inversion. In general, however, the result will be two asymmetric combinations, which we will denote by $\phi^{(0)}$ and $\phi^{(1)}$. When there is asymmetry, it will be assumed that before (and after) mixing, the lowest vibrational state is primarily localized in the lower well, while the next higher state is primarily localized in the upper well (see Figure 1). For large

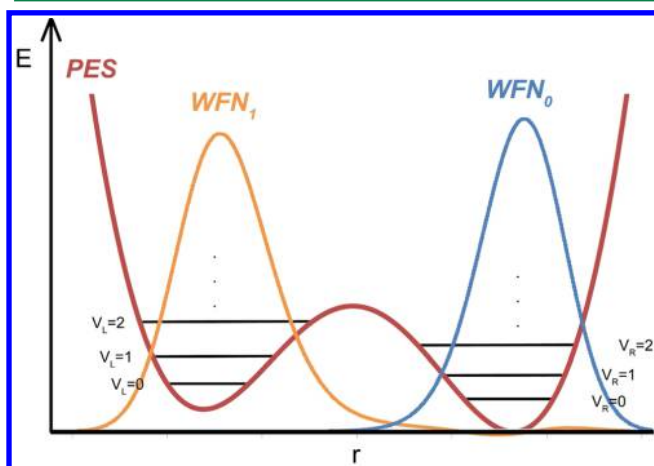


Figure 1. Model of a double-well potential with small asymmetry (PES), together with the two lowest unperturbed wave functions (WFN1).

asymmetry, on the other hand, both the ground and the first excited vibrational state are primarily localized in the lower well. This defines the distinction between small and large asymmetry. Although large asymmetry can be treated as well, we will focus in this paper on the small asymmetry case, and as in ref 16, generalized Van Vleck quasidegenerate perturbation

theory (GVV-PT)^{25–28} will be applied to account for the perturbing effect of an applied electric field on the two states.

We use $\phi^{(0)}$, $\phi^{(1)}$ as the reference space; then, after contributions from higher vibrational states are folded in, the Hamiltonian matrix can be written in the general form

$$\underline{H}(F) = \begin{pmatrix} E^{(00)}(F) & E^{(01)}(F) \\ E^{(10)}(F) & E^{(11)}(F) \end{pmatrix} \quad (1)$$

where F is the electric field and

$$E^{(mn)}(F) = E^{(mn)}(0) - \underline{\mu}^{(mn)} \cdot F - \frac{1}{2} \underline{\alpha}^{(mn)} : \underline{FF} - \frac{1}{6} \underline{\beta}^{(mn)} : \underline{FFF} - \frac{1}{24} \underline{\gamma}^{(mn)} : \underline{FFFF} - \dots \quad (2)$$

with $(m,n) \in \{0,1\}$ and $E^{(01)}(0) = E^{(10)}(0) = 0$. If we assume that the wave functions are real, then $P^{(01)} = P^{(10)}$, for $P = \mu, \alpha, \beta, \gamma$, and $E^{(01)}(F) = E^{(10)}(F)$. Finally, the field-dependent energies are obtained by diagonalizing $\underline{H}(F)$, which yields the two solutions

$$E^{(a,b)}(F) = E^{(+)}(F) \mp \sqrt{[E^{(-)}(F)]^2 + [E^{(01)}(F)]^2} \quad (3)$$

where $E^{(a)}(F)[E^{(b)}(F)]$ is associated with the negative [positive] sign of the square root, and

$$E^{(+)}(F) = \frac{1}{2}(E^{(00)}(F) + E^{(11)}(F)) \quad (4)$$

$$E^{(-)}(F) = \frac{1}{2}(E^{(00)}(F) - E^{(11)}(F)) \quad (5)$$

As recognized in ref 16, the energies $E^{(a)}(F)$ and $E^{(b)}(F)$ cannot be written as a power series in the field, except in certain limiting cases (see below). Nevertheless, it is still possible to define two quantities $A(F)$, $B(F)$, that can be expanded in the field, namely,

$$A(F) = \frac{E^{(a)}(F) + E^{(b)}(F)}{2} = E^{(+)} - \underline{\mu}^{(+)} \cdot F - \frac{1}{2} \underline{\alpha}^{(+)} : \underline{FF} - \frac{1}{6} \underline{\beta}^{(+)} : \underline{FFF} - \frac{1}{24} \underline{\gamma}^{(+)} : \underline{FFFF} + \dots \quad (6)$$

$$B(F) = \frac{(E^{(a)}(F) - E^{(b)}(F))^2}{4} = [E^{(-)}(F)]^2 + [E^{(01)}(F)]^2 = \sum_{n=0} C^{(n)}[n](F)^{[n]} \quad (7)$$

where $P^{(+)} = (P^{(11)} + P^{(00)})/2$ with $P = E, \mu, \alpha, \beta, \gamma$. Here, $(F)^{[n]}$ is a tensor of rank n with components $F_{i_1} F_{i_2} \dots F_{i_n}$, $[n]$ denotes an n -fold contraction, and the tensors $C^{(n)}$ of rank n are given by

$$C^{(0)} = [EE] \quad (8)$$

$$C_i^{(1)} = -2[E\mu]_i \quad (9)$$

$$C_{ij}^{(2)} = -[E\alpha]_{ij} + [\mu\mu]_{ij} \quad (10)$$

$$C_{ijk}^{(3)} = -\frac{2}{3!}[E\beta]_{ijk} + [\mu\alpha]_{ijk} \quad (11)$$

$$C_{ijkl}^{(4)} = -\frac{2}{4!}[E\gamma]_{ijkl} + \frac{1}{4}[\alpha\alpha]_{ijkl} + \frac{1}{3}[\mu\beta]_{ijkl} \quad (12)$$

⋮

$$C^{(n)} = \sum_{n_1=0}^n \frac{1}{n_1!(n-n_1)!} [\Gamma^{n_1} \Gamma^{n-n_1}]_{i_1 \dots i_n} \quad (13)$$

in which $\Gamma^n = -E, \mu, \alpha, \beta, \dots$ for $n = 0, 1, 2, 3, \dots$

$$[\Gamma^{n_1} \Gamma^{n_2}]_{i_1 \dots i_{n_1} j_1 \dots j_{n_2}} = \Gamma_{i_1 \dots i_{n_1}}^{n_1, (-)} \Gamma_{j_1 \dots j_{n_2}}^{n_2, (-)} + \Gamma_{i_1 \dots i_{n_1}}^{n_1, (01)} \Gamma_{j_1 \dots j_{n_2}}^{n_2, (01)} \quad (14)$$

where $\Gamma^{(-)} = (\Gamma^{(00)} - \Gamma^{(11)})/2$.

Eq 6 has been used previously in the context of the limiting case relevant for NH_3 ,^{16,21} but it should be noted that its validity is not restricted to that limit. A is (half) the trace of the Hamiltonian matrix $\underline{H}(F)$ in eq 1. It is one of the two invariants with respect to a unitary transformation of that matrix, the other being the determinant. The determinant also yields a power series in F , but for our purposes, B is more convenient. This latter quantity is essentially the square of the transition frequency ν_{ab} between the two vibrational states and is thus, in principle, experimentally accessible. Indeed, vibrational Stark effect spectroscopy²⁹ is a well-established method to measure the electric field effect on ν_{ab} , although existing analyses consider only single well potentials and have been limited to linear and quadratic terms in the field.

The expansion coefficients in the expression for A are field derivatives of an (average) energy in the limit $F \rightarrow 0$. Thus, these coefficients correspond to the usual definition for the (average) dipole moment and various dipole (hyper)polarizabilities. On the other hand, the coefficients in the expression for B cannot be treated in the same manner. In order to make contact with expressions for the dipole (hyper)polarizabilities as expansion coefficients of a field-dependent energy, we may consider several of the limiting cases alluded to above. One rather trivial limit is obtained if the second term under the square root in eq 3 can be neglected compared to the first term (i.e., the field-induced coupling between the field-free states 0 and 1 is negligible). This leads to separate expansions for each of the states, that is, the energies $E^{(i)}$ depend only on the electric properties of state i . This limit includes some small asymmetry double-well cases with high barriers.

A second limiting case is obtained if the first term under the square root sign in eq 3 is negligible compared to the second, which leads to

$$E^{(a,b)}(F) = E^{(+)}(F) \mp |E^{(01)}(F)| \quad (15)$$

$$\begin{aligned} |E^{(01)}(F)| &= \left| \frac{1}{2} h \nu_{ab}(F) \right| = \left| -\mu^{(01)} \cdot F \right. \\ &\quad \left. - \frac{1}{2} \underline{\alpha}^{(01)} : \underline{FF} - \frac{1}{6} \underline{\beta}^{(01)} : \underline{FFF} - \frac{1}{24} \underline{\gamma}^{(01)} : \underline{FFFF} \right| \end{aligned} \quad (16)$$

This limit implies that at least one of the $P^{(01)}[n]F^n$ terms is very large compared to the zero-field splitting. In this limit, the magnitude of the field-dependent transition frequency $\nu_{ab}(F)$, instead of its square, can be written as a power series in F (assuming that the sign of the power series is retained as a function of the field). This *high-field/medium barrier* limit (see Introduction) applies to the inversion mode of NH_3 .^{16,21} Finally, a third limiting case arises when the second term under the square root in eq 3 is much smaller than the first one—this requires a rather low barrier and/or small asymmetry. In this third limiting case, the splitting is large enough to apply

ordinary nondegenerate perturbation theory. In this *low field/low barrier* case, the state energies can again be written as a power expansion in the field.

2.2. Umbrella Motion in Pyramidal AX_3 Molecules.

The treatment in the previous section is quite general. Here, we specialize the method to the linear and nonlinear electric dipole properties of pyramidal AX_3 molecules. In that case, the occurrence of two equivalent potential wells due to inversion symmetry and an electric field directed along the symmetry axis (taken to be the z -axis), means that the matrix elements $\mu^{(mm)}$ and $\beta^{(mm)}$, with $m \in \{0, 1\}$, as well as $\alpha^{(01)}$ and $\gamma^{(01)}$ are zero. Then, the coefficients $C^{(n)}$ in eqs 8-13 simplify to

$$C^{(2n-1)} = 0 \quad (17)$$

$$C^{(0)} = (E^{(-)})^2 \quad (18)$$

$$C_{zz}^{(2)} = -E^{(-)} \alpha_{zz}^{(-)} + (\mu_z^{(01)})^2 \quad (19)$$

$$C_{zzzz}^{(4)} = -\frac{E^{(-)} \gamma_{zzzz}^{(-)}}{12} + \frac{(\alpha_{zz}^{(-)})^2}{4} + \frac{\mu_z^{(01)} \beta_{zzz}^{(01)}}{3} + \dots \quad (20)$$

The umbrella motion in NH_3 has been treated previously in the high field/medium barrier limit,^{16,21} that is, using eqs 15 and 16. The condition to be fulfilled for the application of this limit was given as $(\mu_z^{(01)} F_z)^2 \gg (E^{(-)})^2$. It is sufficient under the implicit assumption that the (hyper)polarizabilities do not affect this inequality. More rigorously, we require that $|E^{(01)}(F)| \gg |E^{(-)}(F)|$ or, equivalently

$$\begin{aligned} &\left| \mu_z^{(01)} F_z + \frac{1}{6} \beta_{zzz}^{(01)} F_z^3 + \dots \right| \\ &\gg \left| E^{(-)} - \frac{1}{2} \alpha_{zz}^{(-)} F_z^2 - \frac{1}{24} \gamma_{zzzz}^{(-)} F_z^4 - \dots \right| \end{aligned} \quad (21)$$

Finally, for pyramidal AX_3 molecules, the expression for A (eq 6) simplifies to

$$A = E^{(+)}(0) - \frac{1}{2} \alpha_{zz}^{(+)} F_z^2 - \frac{1}{24} \gamma_{zzzz}^{(+)} F_z^4 + \dots \quad (22)$$

3. METHODS

The methodology employed to solve the vibrational Schrödinger equation for CH_3^- closely follows the treatment of NH_3 in ref 21 and is, thus, briefly summarized. Curvilinear coordinates are employed to describe the vibrational displacements (particularly, the inversion motion). The programs TNUM,³⁰ which determines the kinetic energy operator numerically, and ELVIBROT³¹ developed by Lauvergnat and Nauts, are then used to compute zero-point vibrationally averaged energies and properties. We separate the vibrational coordinates into an active set q_{act} , that is treated explicitly, and an inactive set q_{inact} , treated in a more approximate way. As in refs 16 and 21, the active coordinate θ , which describes the inversion motion, is taken to have the form originally introduced by Handy et al.³² Thus, it is defined by the three angles θ_1 , θ_2 , and θ_3 spanned by the N-H bonds and the trisector axis:

$$\theta = \frac{1}{3}(\theta_1 + \theta_2 + \theta_3) - \frac{\pi}{2} \quad (23)$$

The remaining coordinates were chosen to be inactive (see later) and three different models were considered for their

Table 1. Comparison of Coefficients $C^{(n)}$, $n = 2, 4$ (in au^2) Calculated from the Full Expression Equations 17–20 ('Full') and the High-Field/Medium Barrier Limit ('Limit') of NH_3 at MP2/Pol Level of Theory^a

	1D		(1 + 5)D HADA		(1 + 5)D cHAC	
	full	limit ^b	full	limit ^b	full	limit ^b
$C_{zz}^{(2)}$	0.3529	0.3529	0.3613	0.3613	0.3617	0.3617
$C_{zzzz}^{(4)}$	−50.53	−50.58	−41.73	−41.62	−41.61	−41.49
$\mu_z^{(01)}$		0.5941 (0.5941)		0.6011 (0.6009)		0.6014 (0.6012)
$\beta_{zzz}^{(01)}$		−255.4 (−256.4)		−207.7 (−207.3)		−207.0 (−206.6)

^aThe numbers in brackets are from ref 21; dipole moments and hyperpolarizabilities are in au. ^bThe coefficients $C^{(n)}$ in the 'Limit' approximation were computed from eqs 17–20, neglecting all terms containing $P^{(-)}$ and using $\mu^{(01)}$ and $\beta^{(01)}$ obtained from a fit to eqs 15 and 16, or the equivalent equations for the dipole moments instead of the energies

treatment. In each of these models, the inactive coordinates are optimized by energy minimization for each value of θ . Our least accurate 1D *flexible* model uses the inversion potential determined at this optimized geometry, V_0 , to form the 1D Schrödinger equation, which is solved numerically using ELVIBROT. The other two approximations introduce the notion of harmonic adiabatic channels. For these models, we add the harmonic potential energy term $V_2(q_{\text{inact}}; q_{\text{act}})$, for the contribution of the inactive coordinates along the minimum energy path described above. Accordingly, the total nuclear wave function is expressed as^{33,34}

$$\psi(q_{\text{act}}, q_{\text{inact}}) = \sum_{iu} c_{iu} \phi_i(q_{\text{act}}) \phi_u(q_{\text{inact}}; q_{\text{act}}) \quad (24)$$

where $\phi_u(q_{\text{inact}}; q_{\text{act}})$ is an eigenfunction for the inactive coordinates parametrized by the active coordinate. After an integration over the inactive variables, one obtains an effective Hamiltonian matrix $H_{uw}(q_{\text{act}}; \partial/\partial q_{\text{act}})$, which acts only on the n active variables q_{act} . Neglecting all H_{uw} with $w \neq u$ one obtains an effective equation for each adiabatic state. This model is called the $(n + m)$ D *harmonic adiabatic approximation* (HADA),^{33,34} where $n + m = 3N - 6$. If the off-diagonal terms are included, the *coupled harmonic adiabatic channels approximation* (cHAC) is obtained.³⁴

The three models employed will thus be designated 1D, (1 + 5)D HADA and (1 + 5)D cHAC. In ref 21, a 2D model was employed as well, together with the corresponding HADA and cHAC models, using the symmetric stretch as the second active coordinate. Since this led to results that differ little from those obtained with the (1 + 5)D models, and they are computationally rather expensive, the previous 2D models were not used here. An indication that the symmetric stretch is even less important for CH_3^- is the fact that the change of the C–H bond length between the optimized planar structure and the fully optimized geometry is only 0.014 Å (at the MP2/daug-cc-CVTZ level) as compared to the corresponding change in the N–H bond length of 0.023 Å (at the MP2/Sadlej level).

The energies $E^{(a)}(F)$ and $E^{(b)}(F)$ are computed using different field strengths and the coefficients $C^{(n)}$, $\alpha^{(+)}$, ... are, then, obtained by numerical differentiation of the quantities A and B according to eqs 6 and 7, respectively. The coefficients $\alpha^{(+)}$ and $\gamma^{(+)}$ can also be obtained from the average of the field-dependent dipole moments $(\mu^{(a)} + \mu^{(b)})/2$, which is used as a crosscheck. Unfortunately, there is no corresponding relationship for B . Another difference between the coefficients in the electric field expansions of A versus B is that the former can be separated into electronic and vibrational contributions,²¹ whereas the occurrence of products of electrical properties in the $C^{(n)}$ coefficients means that they contain nonseparable vibrational-electronic cross-terms.

All electronic structure calculations and geometry optimizations were done with Gaussian 09.³⁵

4. RESULTS AND DISCUSSION

4.1. NH_3 Reconsidered. In a first application, the umbrella motion in NH_3 was reconsidered with the generalized eqs 17–20, to validate the results of refs 16 and 21, where this system was treated in the approximate high-field/medium barrier limit (eqs 15, 16). In Table 1, the results from both the full (eqs 17–20) and the approximate (eqs 15 and 16) treatment are compared for the potential energy surface (PES) and Hessian surfaces computed at the MP2 level with Sadlej's Pol basis set.³⁶ The coefficients $C^{(n)}$ in the approximate treatment were computed from eqs 17–20, neglecting $E^{(-)}$, $\alpha_{zz}^{(-)}$, and $\gamma_{zzzz}^{(-)}$ as in our earlier work. Moreover, the quantities $\mu^{(01)}$ and $\beta^{(01)}$ were obtained from a fit to eqs 15 and 16, or the equivalent equations for the dipole moments. Very good agreement between both treatments was found for $C_{zz}^{(2)}$ and $C_{zzzz}^{(4)}$, which justifies the assumptions made previously, including the implicit ones mentioned in section 2.2 (see eq 21).

4.2. CH_3^- . The anion CH_3^- is an unstable molecule with a theoretically predicted^{22,37} pyramidal structure such as NH_3 but with a considerably lower potential barrier for inversion. This means that the high-field/medium barrier limit is likely not to be applicable, which suggests use of the extended treatment developed in section 2, and makes the NLO properties of this molecule of interest for our purposes. In the numerical approach applied here, the inversion motion is computed step by step along the inversion coordinate and at each point a geometry optimization is performed for all other coordinates. According to multireference CASSCF calculations, the Born–Oppenheimer approximation becomes invalid at some point along the inversion motion, as the ground state of CH_3^- comes energetically close to excited Rydberg states.²² No attempt has been made to tackle this additional complication; the potential energy surface has been treated entirely under the Born–Oppenheimer approximation.

Calculation of the (hyper)polarizabilities of free anions generally requires diffuse basis sets. This is also the case for CH_3^- , as shown in Table 2, where we report MP2 electronic properties along the symmetry axis (pointing from the C atom to the hydrogens), computed for several of Dunning's correlation-consistent basis functions^{38–41} using the geometry optimized separately for each basis set. The values are roughly converged for the d-aug-cc-pVTZ basis set (cf. d-aug-cc-pVQZ) although the convergence becomes worse with increasing order of the property. In view of previous experience concerning the necessity of an accurate description of core correlation (in addition to valence correlation) for vibrational energies,^{21,34} we

Table 2. Electronic Dipole Moment and Diagonal (Hyper)Polarizabilities of CH_3^- along the Symmetry Axis Computed at the MP2 Level with Different Basis Sets ([d]aVXZ= [d-]aug-cc-pVXZ with $X = \text{T, Q, S}$; daCVTZ=d-aug-cc-pCVTZ)^a

	aVTZ	aVQZ	aVSZ	daVTZ	daVQZ	daCVTZ
μ_z^{el}	0.5311	0.5143	0.5077	0.4810	0.4793	0.4780
α_{zz}^{el}	165.31	197.45	236.72	561.9	563.77	561.59
β_{zzz}^{el}	7605.0	10518	13440	41020	45951	41100
$\gamma_{zzzz}^{\text{el}}/10^4$	24.0	104.8	234.5	15156	17616	15171

^aAll quantities are in au.

finally chose the d-aug-cc-pCVTZ basis set. The 1s electrons of the carbon atom were correlated in all calculations. The geometry of CH_3^- at the MP2/daug-cc-pCVTZ level is characterized by a C–H distance of 1.094 Å and an H–C–H bond angle of 112.09 degrees, which agrees reasonably well with previous results.²² As the purpose here is to show the application of the new treatment, rather than accurately compute the NLO properties of CH_3^- , we do not explore the effect of electronic correlation beyond the MP2 level. In addition to CH_3^- we also examine the isotopically substituted anion CT_3^- at the same level of treatment. The latter provides an example with a different barrier/tunneling splitting.

For ions, the dipole moment determined from the field-dependent energies, is origin-dependent. A unique choice of the origin at the center of mass is enforced by the Eckart conditions in our calculations. Thus, all properties and energies are referred here to the center of mass. Note that the rotational Eckart conditions must be satisfied in carrying out the field-dependent geometry optimizations used to compute the total (i.e., electronic+vibrational) (non)linear properties.⁴²

In Table 3, we show the first few vibrational energies of the inversion mode in CH_3^- and CT_3^- calculated for our three different models. The calculated ‘classical’ inversion barrier, defined as the difference between the top of the barrier and the minimum of the potential well, is 396 cm^{-1} with the lowest CH_3^- vibrational level, 0^+ , at approximately 238 cm^{-1} (183 cm^{-1} for CT_3^-) above the minimum. For CH_3^- only the lowest two levels 0^+ and 0^- are below the top of the barrier. This is in agreement with previous calculations,²² which combined an all-valence CISD electronic structure treatment with an augmented van Duijneveldt basis set and an empirical anharmonic fit-function,⁴³ although the classical inversion barrier at that level was considerably higher (740 cm^{-1}). Thus, also the tunneling splitting at the CISD level is considerably smaller than the one

computed here at the MP2 level, although higher vibrational levels are in more reasonable agreement (see Table 3). The $0^- - 1^+$ energy level difference in CH_3^- has been estimated from photoelectron spectra to be $460 \pm 40 \text{ cm}^{-1}$.⁴⁴ Our value of 405 cm^{-1} appears to be a bit too low at the current level of approximation. The tunneling splitting between the two lowest levels depends sensitively on the model used for the vibrational description: for both CH_3^- and CT_3^- the value obtained for the relaxed 1D model is nearly twice that obtained for the harmonic adiabatic channels models. However, the 1 + 5D HADA and 1 + 5D cHAC results show nice agreement. The splitting in CH_3^- is much larger at the MP2 level (more than a factor of 50) than in NH_3 , where it is 0.79 cm^{-1} .⁴⁵ This is a consequence of the much lower potential barrier for inversion in CH_3^- . We note that the best splitting reported by Kraemer et al.²² (computed at the CISD level with an augmented van Duijneveldt basis set and empirical potential functions), is about a factor of 3 lower than our cHAC/HADA values.

The total (electronic + vibrational) static electric dipole properties of CH_3^- and CT_3^- obtained with the new treatment are shown in Table 4. They were computed using Romberg differentiation^{46,47} with applied electric field strengths between $\pm 0.00025 \text{ au}$ and $\pm 0.008 \text{ au}$ along the C_3 axis. Due to the large magnitude of the properties, the window of applicable field strengths is rather small. In order to obtain a sufficient number of points for the Romberg fit, a nonstandard ratio of step sizes, that is, $2^{1/4}$ (rather than 2), was used according to the treatment of Medved et al.^{48,49} As observed for NH_3 , the coefficients $C_{zz}^{(2)}$ and $C_{zzzz}^{(4)}$ as well as $\alpha_{zz}^{(+)}$ and $\gamma_{zzzz}^{(+)}$ could be determined with good accuracy for both isotopic species.

Employing the full dimensional harmonic adiabatic channel approximations, instead of the relaxed 1D model, has quite a large effect on nearly all of the coefficients. $C_{zz}^{(2)}$ changes by a moderate 7–8% for the 1D model with respect to the (1 + 5)D cHAC values, but $C_{zzzz}^{(4)}$ changes by 32–39%, $\alpha_{zz}^{(+)}$ by 20–26% and $\gamma_{zzzz}^{(+)}$ by 16–40%. As observed for NH_3 ,²¹ there is little difference between the properties obtained with either the HADA or the cHAC approximation; the largest difference (4%) is found for $\gamma_{zzzz}^{(+)}$ of CH_3^- .

In attempting to evaluate the NLO properties assuming the high field/medium barrier limit, we found that the Romberg procedure does not give any range of field values where the properties can safely be considered as constant. We take this to be a sign that the high field/medium barrier limit is not applicable here. Nevertheless, using the values with the smallest variations, we obtain $\mu_z^{\text{lim}} = 0.429 \text{ au}$ (0.427 au) and $\beta_{zzz}^{\text{lim}} = -233800 \text{ au}$ (–204000 au) for CH_3^- (CT_3^-) in the (1 + 5)D

Table 3. Vibrational Energies of CH_3^- and CT_3^- (in cm^{-1}) Computed at the MP2 Level with the d-aug-cc-pCVTZ Basis

level	CH ₃ ⁻			lit. ^a	CT ₃ ⁻		
	(1 + 5)D				(1 + 5)D		
	1D	HADA	cHAC		1D	HADA	cHAC
0 ⁺	0	0	0	0	0	0	0
0 ⁻	76.09	43.55	43.01	19	17.30	8.36	8.26
1 ⁺	444.08	451.33	449.64	533	279.19	312.50	311.99
1 ⁻	773.23	737.12	732.58	769	428.28	426.26	424.39
2 ⁺	1187.00	1141.04	1133.18	1190	663.47	660.48	657.25
2 ⁻	1640.31	1580.97	1568.49	1639	916.21	900.58	894.98
3 ⁺	2131.15	2062.42			1195.28	1172.63	
3 ⁻	2653.19	2576.69			1494.04	1465.02	

^aRef 22.

Table 4. Coefficients $C^{(n)}$, $n = 2, 4$ (in au^2), and $\alpha_{zz}^{(+)}$, $\gamma_{zzzz}^{(+)}$ (au) Obtained for CH_3^- and CT_3^- , at the MP2 Level with the d-aug-cc-pCVTZ Basis^a

	CH_3^-			CT_3^-		
	(1 + 5)D			(1 + 5)D		
	1D	HADA	cHAC	1D	HADA	cHAC
$C_{zz}^{(2)}$	0.1518	0.1545 (0.184)	0.1549	0.1681	0.1799 (0.182)	0.1802
$C_{zzzz}^{(4)}$	−26328	−20105 (−33400)	−20150	−32770	−23610 (−29100)	−23580
$\alpha_{zz}^{(+)}$	805.23	641.88	640.77	749.25	624.90	623.66
$\gamma_{zzzz}^{(+)}/10^8$	4.95	4.45	4.27	6.48	4.64	4.63

^aValues in brackets are obtained in the high field/medium barrier limit (see text).

HADA model, which leads to $C^{(2)} = 0.184$ au (0.182 au) and $C^{(4)} = -33400$ au (−29100 au), when all terms containing $E^{(-)}$, $\alpha_{zz}^{(-)}$, and $\gamma_{zzzz}^{(-)}$ are neglected as appropriate for this limit. Comparison with the values from the full treatment in Table 4, (i.e., $C^{(2)} = 0.155$ au, $C^{(4)} = -20105$ au for CH_3^- , $C^{(2)} = 0.180$ au, $C^{(4)} = -23600$ au for CT_3^-), shows that the discrepancies are indeed quite large for $C^{(2)}$ and $C^{(4)}$ of CH_3^- and $C^{(4)}$ of CT_3^- , while $C^{(2)}$ of CT_3^- is in good agreement. The smaller discrepancies between the full treatment and the high field/medium barrier limit found for CT_3^- are a result of the smaller inversion splitting of CT_3^- as compared to that of CH_3^- . Thus, $\alpha_{zz}^{(-)}$, and $\gamma_{zzzz}^{(-)}$ can not be neglected and the high field/medium barrier is inapplicable. The value μ_z^{lim} of CH_3^- is in good agreement with the analytical value computed by ELVIBROT (0.430 au). We can, thus, use the former value of the dipole moment to show that the reverse inequality in eq 21 is also not valid. For the range of fields used here, the right-hand side of eq 21, truncated to first order, varies from 0.00001 to 0.0034 au, which is of comparable magnitude to $|E^{(-)}| = 0.0002$ au. This clearly indicates that the low barrier limit mentioned in Section 2.1 does not apply.

Finally, comparison of the total values of $\alpha_{zz}^{(+)}$ with the electronic value in Table 2 shows that the vibrational contribution to $\alpha_{zz}^{(+)}$ is relatively modest (10–12% at the HADA/cHAC levels). On the other hand, the vibrational part of $\gamma_{zzzz}^{(+)}$ contributes about 2/3 of the full value. As mentioned above, a corresponding analysis is not possible for the $C^{(n)}$ coefficients.

5. SUMMARY

In this work, we presented a method for computing the nonlinear optical properties of molecules with arbitrary double-well potentials. The cases of either small asymmetry or perfect symmetry were treated explicitly. In order to be valid for the whole range of potential barriers, the usual power series expansion of the energy in the field has to be abandoned. Although the average energy for the lowest pair of levels that are split by tunneling can still be expressed as a power series expansion, such is not the case for the individual state energies. We have shown, however, that there is another quantity, namely the square of the splitting energy, that can be conveniently written as a power series in the field, and whose coefficients can be expressed in terms of the transition dipole moments and (hyper)polarizabilities, as well as the difference of these properties between the two lowest states, which are missing in the average energy expression. The usual expansion of the individual energy levels can, in turn, be recovered for the limiting cases treated previously.

The new quantity is, in principle, measurable by vibrational Stark effect spectroscopy (VSES). Current treatments of VSES,

however, are restricted to single well potentials and consider only up to quadratic terms in the field. It remains to develop a protocol for obtaining the nonlinear optical coefficients presented here from experimental measurements. If this turns out to be feasible, it would be one of the few experimental methods available to directly determine static NLO properties.

The new formulation was applied to two molecules with large amplitude inversion motions, NH_3 and CH_3^- . For ammonia, we verified the validity of our previous treatment of this molecule in the medium barrier/large field limit, which allows the individual state energies to be written as an ordinary power series expansion. For the inversion of CH_3^- , which cannot be treated consistently in any of the limiting cases, we could show that the new treatment gives reliable and consistent results at the level employed (MP2).

Although restricted to double-well potentials here, we believe that our formulation can be extended to multiwell potentials. Moreover, the new treatment is, presently, restricted to static electric fields. We plan to attack both of these extensions in future work.

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Notes

The authors declare no competing financial interest.

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