

# A New Way of Analyzing Vibrational Spectra. I. Derivation of Adiabatic Internal Modes

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*Received 24 March 1997; revised 30 September 1997; accepted 8 October 1997*

**ABSTRACT:** A new way of analyzing measured or calculated vibrational spectra in terms of internal vibrational modes associated with the internal parameters used to describe geometry and conformation of a molecule is described. The internal modes are determined by solving the Euler–Lagrange equations for molecular fragments  $\phi_n$  described by internal parameters  $\zeta_n$ . An internal mode is localized in a molecular fragment by describing the rest of the molecule as a collection of massless points that just define molecular geometry. Alternatively, one can consider the new fragment motions as motions that are obtained after relaxing all parts of the vibrating molecule but the fragment under consideration. Because of this property, the internal modes are called adiabatic internal modes, and the associated force constants  $k_a$ , adiabatic force constants. Minimization of the kinetic energy of the vibrating fragment  $\phi_n$  yields the adiabatic mass  $m_a$  (corresponding to  $1/G_{nn}$  of Wilson's  $G$  matrix) and, by this, adiabatic frequencies  $\omega_a$ . Adiabatic modes are perfectly suited to analyze and understand the vibrational spectra of a molecule in terms of internal parameter modes in the same way as one understands molecular geometry in terms of internal coordinates. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* 67: 1–9, 1998

## Introduction

Vibrational spectroscopy is one of the most useful experimental tools for describing structural and electronic features of molecules

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Contract grant sponsor: Swedish Natural Science Research Council (NFR).

[1–9]. The pattern of infrared (IR) or Raman bands in a vibrational spectrum is directly related to the bond pattern in a molecule, i.e., molecular structure, while the exact positions of the individual bands reflect properties of the chemical bonds and the electronic structure of the molecule. In principle, it should be possible to characterize each bond of the molecule by an appropriate stretching frequency and stretching force constant once the vibrational spectra of the molecule in question are

known. This should also hold for any three- or four-atom unit in a molecule provided that one knows the corresponding properties of bending and torsional motions. Chemists have learned to understand the geometry and conformation of a molecule in terms of internal coordinates such as bond lengths, bond angles, and torsional angles. Therefore, it would be chemically rewarding to relate vibrational frequencies and force constants to internal coordinates  $q_n$  or any other suitable internal parameter  $\zeta_n$ , each of which is connected with a two-, three-, or  $n$ -heavy atom unit  $\phi_n$  of the molecule.

There are two major reasons why the measurement of the vibrational spectra of a molecule does not automatically lead to a description of its electronic structure, its bonding pattern, and its geometry: First, a normal mode analysis of a measured vibrational spectrum requires knowledge of the full force constant matrix which in the normal case is not available [1–6]. Second, even if the force constant matrix is known, the normal mode analysis will lead to “delocalized” molecular motions (expressed in normal mode coordinates  $Q$ ), each of which involves several atoms that not necessarily form a chemically interesting unit. Therefore, it is generally difficult to extract out of the normal mode analysis chemically useful frequencies and force constants of well-defined subunits of the molecule.

In this and the following articles, we will demonstrate with the help of *ab initio* calculations that it is possible to derive largely “localized” molecular motions, each of which is associated with a particular internal parameter that can be an internal coordinate or any other useful coordinate. For this purpose, we describe a new way of analyzing and describing the normal modes of a molecule in terms of *internal motions* where the latter term emphasizes that each motion is associated with a specific internal parameter. The information gained from this analysis leads to a direct description of bonding in a molecule and a detailed analysis of electronic structure. We will show in the following articles how this information can be used to describe geometrical features and other molecular properties on the basis of a combination of IR/Raman measurements and *ab initio* vibrational frequency calculations. This procedure will be developed in the same spirit as that of the NMR/*ab initio*/chemical shift method for the determination of molecular geometries [10].

We will proceed in the present article in the following way: In the next section, we present the leading parameter principle that provides a basis for relating molecular properties to internal parameters and, accordingly, represents the starting point for developing the concept of internal vibrational modes. In the third section, the theory of the adiabatic mode vectors is developed as the most logical choice for the definition of internal vibrational modes. The adiabatic principle is applied to the commonly used harmonic approximation of vibrational modes and adiabatic mode vectors are derived from the normal modes of vibrational spectroscopy (the fourth section). Finally, in the fifth section, internal force constants, internal masses, and internal frequencies are determined for internal modes in general and adiabatic modes specifically.

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## Leading Parameter Principle and the Concept of Internal Vibrations

If the nuclei of a molecule are displaced by  $\Delta x$  from their equilibrium positions  $x_0$  ( $x$ : column vector containing the  $3K$  Cartesian nuclear coordinates  $x_i$ ;  $K$ : number of atoms), the corresponding change in an internal parameter  $\zeta_n$  associated with the molecular fragment  $\phi_n$  will be given by

$$\Delta \zeta_n = \sum_{i=1}^{3K} B_{ni} \Delta x_i, \quad (1)$$

where  $B_{ni}$  is an element of the “B-matrix” [1]:

$$B_{ni} = \left( \frac{\partial \zeta_n(\mathbf{x})}{\partial x_i} \right)_{\mathbf{x}=\mathbf{x}_0}. \quad (2)$$

Parameter  $\zeta_n(\mathbf{x})$  is defined by the choice of a suitable set of coordinates describing the molecule (internal coordinates, normal coordinates, symmetry coordinates, puckering coordinates [11], delocalized coordinates [12], curvilinear coordinates, etc.). Apart from this, the term *internal parameter* is used to emphasize the dual role coordinates play in this work. First, they are used to describe the configuration space, which relates to the fact that  $3K - 6$  coordinates are needed to define molecular geometry in the general case. Second, each internal parameter defines a specific molecular fragment and, therefore, can be used to describe the properties (energy, dipole moment vector, polarizability

tensor, etc.) of this fragment independently of how the total configuration space is spanned.

Once  $\zeta_n(\mathbf{x})$  has been defined, only those nuclear displacements are considered, which lead to a change in  $\zeta_n(\mathbf{x})$  equal to constant  $\Delta\zeta_n^*$ :

$$\Delta\zeta_n^* = \sum_{i=1}^{3K} B_{ni} \Delta x_i^*. \quad (3)$$

Clearly,  $\Delta\zeta_n^*$  should be chosen in such a way that fragment  $\phi_n$  can be described in the best way possible. Since Eq. (3) does not uniquely define the displacement vector  $\Delta\mathbf{x}^*$ , an additional condition is needed so that the direction of the vector  $\mathbf{v}_n$  in Eq. (4) is selected,

$$\Delta\mathbf{x}^* = \mathbf{v}_n \Delta\zeta_n^*, \quad (4)$$

where the choice of the displacement vector  $\mathbf{v}_n$  is based on chemical convenience as will be discussed in the following sections. Equations (3) and (4) lead to the normalization condition for  $\mathbf{v}_n$ :

$$1 = \sum_{i=1}^{3K} B_{ni} (\mathbf{v}_n)_i, \quad (5)$$

where  $(\mathbf{v}_n)_i$  is the  $i$ th component of vector  $\mathbf{v}_n$ .

With the help of Eqs. (4) and (5), it is possible to associate the vector  $\mathbf{v}_n$  with the molecular fragment  $\phi_n$ . In the sense of Eq. (4), one can say that a single parameter  $\zeta_n^*$  determines (*leads*) the displacements of the nuclei of fragment  $\phi_n$ . Hence,  $\zeta_n^*$  can be called the *leading parameter* of the internal molecular motion described by  $\mathbf{v}_n$  and Eq. (4) represents what one may call a *leading parameter principle*.

To define the vibrational vector  $\mathbf{v}_n$ , the leading parameter principle has to be complemented by a condition that reflects the dynamical aspects of a nuclear motion and the properties of the molecular energy  $E(\mathbf{x})$ . The internal parameter  $\zeta_n$  localizes the vibration within a molecular fragment and  $E(\mathbf{x})$  can be used to combine localization of the internal mode with dynamical balance. For example, one can require that the displacement forces accompanying the vibration concentrate within a molecular fragment  $\phi_n$ , i.e., outside the fragment the forces exerted on the nuclei vanish so that the latter adopt an equilibrium position typical of the situation of the vibrating fragment.

A vibration that is localized within a certain molecular fragment  $\phi_n$  will be called an *internal vibration*. Accordingly,  $\mathbf{v}_n$  will be called an *internal*

*vibration vector* or an *internal displacement vector*. Once an internal displacement vector  $\mathbf{v}_n$  has been determined, it is possible to calculate quantities such as the *internal force constant*  $k_n$ , the *internal mass*  $m_n$ , and, thereby, the *internal frequency*  $\omega_n$ . The quantities  $k_n$ ,  $m_n$ , and  $\omega_n$  can be used to characterize the fragment  $\phi_n$  associated with the pair  $(\zeta_n^*, \mathbf{v}_n)$ . If  $\zeta_n$  is chosen as an internal coordinate  $q_n$  such as the bond length or bond angle, then  $\phi_n$  will correspond to a diatomic or triatomic molecular fragment chemically defined by the internal coordinates in question. Motions of these fragments are bond stretching and angle bending, respectively. The dynamics of the molecule can be described in terms of localized internal modes such as bond stretching, angle bending, etc., associated with simple internal coordinates  $q_n$  (internal parameters  $\zeta_n$ ) rather than complicated combinations of Cartesian or internal coordinates as, e.g., the normal coordinates. This will facilitate the description and understanding of the dynamic motions of a molecule, in particular, since it connects dynamic properties of the molecule with bond (or other group) properties.

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## Definition of Adiabatic Internal Vibrations

In the following derivation, we abbreviate the differences  $\Delta\mathbf{x}$ ,  $\Delta\zeta$ , etc., by  $\mathbf{x}$ ,  $\zeta$ , etc., for reasons of simplicity. The dynamics of the nuclei of a molecule can be determined by solving the Euler–Lagrange Eqs. (6):

$$\frac{d}{dt} \frac{\partial L(\mathbf{x}, \dot{\mathbf{x}})}{\partial \dot{x}_i} - \frac{\partial L(\mathbf{x}, \dot{\mathbf{x}})}{\partial x_i} = 0, \quad i = 1, \dots, 3K, \quad (6)$$

where  $L(\mathbf{x}, \dot{\mathbf{x}}) = T(\dot{\mathbf{x}}) - V(\mathbf{x})$  is the Lagrangian;  $T(\dot{\mathbf{x}})$ , the kinetic energy,

$$T(\dot{\mathbf{x}}) = \frac{1}{2} \dot{\mathbf{x}}^+ \mathbf{M} \dot{\mathbf{x}} \quad (7)$$

( $\mathbf{M}$ : mass matrix with elements  $m_i$ ); and  $V(\mathbf{x})$ , the potential energy function of the molecule

$$V(\mathbf{x}) = \frac{1}{2} \mathbf{x}^+ \mathbf{f} \mathbf{x}, \quad (8)$$

which is obtained by expanding  $E(\mathbf{x})$  in a Taylor series and neglecting terms higher than to second order.

The solutions of (6) take the form of (9) [1-6]:

$$\mathbf{x} = \mathbf{I}_\mu Q_\mu, \quad (9)$$

where  $Q_\mu$  is a normal coordinate, which oscillates with the frequency  $\omega_\mu$  according to (10):

$$Q_\mu(t) = a \cos(\omega_\mu t) + b \sin(\omega_\mu t). \quad (10)$$

Inserting (8) and (9) into (7) leads to the basic equation of vibrational spectroscopy [1-6]:

$$\mathbf{f}\mathbf{l}_\mu = \omega_\mu^2 \mathbf{M}\mathbf{l}_\mu, \quad \mu = 1, \dots, N_{vib}, \quad (11)$$

which is used to calculate the  $N_{vib} = 3K - L$  normal mode frequencies of a  $K$ -atomic molecule, where  $L$  gives the number of zero eigenvalues in (11) resulting from translations and rotations of the molecule.

Equations (4) and (9) are closely related since the normal coordinate  $Q_\mu$  corresponds to the leading parameter  $\zeta_n^*$ , and  $\mathbf{l}_\mu$ , to the internal motion  $\mathbf{v}_n$ . The only difference between (4) and (9) is that the normal mode vectors  $\mathbf{l}_\mu$  are determined by Eq. (11) while the nuclear displacement vectors  $\mathbf{v}_n$  are chosen according to chemical criteria. The time dependence of  $\zeta_n^*$  in (4) will be of the same form as in (10) with the normal mode frequency  $\omega_\mu$  being replaced by the internal frequency  $\omega_n$ .

In vibrational spectroscopy, it is of advantage to express Eq. (11) in terms of  $N$  internal coordinates  $q_n$  [collected in the column vector  $\mathbf{q} = (q_1, \dots, q_n)^+$ ] rather than Cartesian coordinates  $\mathbf{x}$ . To specify the position of all nuclei in Cartesian space, an additional set of  $L$  external coordinates  $e_i$  [collected in the column vector  $\mathbf{e} = (e_1, \dots, e_L)^+$ ] has to be given. The transformation from internal coordinates to Cartesian is given by Eq. (12) [13]:

$$x_i = \sum_{m=1}^N C_{im} q_m + \sum_{\alpha=1}^L C_{0,i\alpha} e_\alpha, \quad (12)$$

where  $C_{im}$  is an element of the  $(3K, N)$ -rectangular matrix  $\mathbf{C}$ :

$$\mathbf{C} = \mathbf{M}^{-1} \mathbf{B}^+ \mathbf{G}^{-1}, \quad (13)$$

with  $\mathbf{G}$  being Wilson's  $G$ -Matrix [1]:

$$\mathbf{G} = \mathbf{B} \mathbf{M}^{-1} \mathbf{B}^+. \quad (14)$$

Matrix  $\mathbf{C}_0$  was defined by Neto [13]. The following relationships hold:

$$\mathbf{B}\mathbf{C} = \mathbf{I} \quad (15)$$

and

$$\mathbf{B}\mathbf{C}_0 = \mathbf{0}. \quad (16)$$

The Lagrangian can be expressed according to  $L = L_{int} + L_{ext}$ , where  $L_{ext}$  depends on external coordinates and, therefore, is not relevant for the vibrational problem.  $L_{int}$  determines the time dependence of the internal coordinates and is given by

$$L_{int}(\mathbf{q}, \dot{\mathbf{q}}) = \frac{1}{2} \dot{\mathbf{q}}^+ \mathbf{G}^{-1} \dot{\mathbf{q}} - \frac{1}{2} \mathbf{q}^+ \mathbf{F} \mathbf{q}, \quad (17)$$

where  $\mathbf{F}$  ( $N \times N$ ) is the force constant matrix in internal coordinates with elements (18):

$$F_{nm} = \mathbf{c}_n^+ \mathbf{f} \mathbf{c}_m, \quad (18)$$

with  $\mathbf{c}_m$  being a column vector of matrix  $\mathbf{C}$ . Solution of the Euler-Lagrange Eqs. (19)

$$p_m = \frac{\partial L_{int}(\mathbf{q}, \dot{\mathbf{q}})}{\partial \dot{q}_m} \quad (19a)$$

$$\frac{d}{dt} p_m = \frac{\partial L_{int}(\mathbf{q}, \dot{\mathbf{q}})}{\partial q_m} \quad (19b)$$

( $p_m$ : generalized momentum) leads to Wilson's GF formalism for determining vibrational frequencies  $\omega_\mu$  [1]:

$$\mathbf{F} \mathbf{d}_\mu = \omega_\mu^2 \mathbf{G}^{-1} \mathbf{d}_\mu, \quad (20)$$

$$\omega_\mu^2 = \frac{\mathbf{d}_\mu^+ \mathbf{F} \mathbf{d}_\mu}{\mathbf{d}_\mu^+ \mathbf{G}^{-1} \mathbf{d}_\mu}. \quad (21)$$

Vector  $\mathbf{d}_\mu$  represents the normal mode  $\mu$  in internal coordinate space. It can be transformed to Cartesian coordinate space according to Eq. (22):

$$\mathbf{l}_\mu = \mathbf{C} \mathbf{d}_\mu. \quad (22)$$

One could assume that  $(\mathbf{d}_\mu)_n = \delta_{n\mu}$  ( $\delta_{n\mu}$ : Kronecker delta) since this leads to  $\mathbf{l}_\mu = \mathbf{c}_n$  for  $\mu = n$ . However, even if displacements along vectors  $\mathbf{c}_n$  and  $\mathbf{c}_m$  do not couple, thus leading to a diagonal  $\mathbf{F}$  matrix with  $F_{nm} = 0$  (no electronic coupling), there is always mass coupling between the vectors  $\mathbf{c}$  because the  $\mathbf{G}$  matrix is nondiagonal, which according to Eq.(20) leads to  $d_{n\mu} \neq \delta_{n\mu}$  and  $\mathbf{l}_\mu \neq \mathbf{c}_n$ .

Nevertheless, most vibrational spectroscopists will assume a more diagonal character of the  $\mathbf{G}$  matrix if there is a large mass difference between the atoms participating in the molecular motions. In some way, the assumption  $\mathbf{I}_\mu = \mathbf{c}_n$  provides the only basis for an experimentalist to discuss measured frequencies in terms of internal mode frequencies, thus implying that  $\mathbf{v}_n = \mathbf{c}_n$ . However,  $\mathbf{v}_n = \mathbf{c}_n$  is not a satisfactory choice of an internal vibration as will be shown in the following article [14].

To obtain an internal vibrational mode  $\mathbf{v}_n$  associated with the internal parameter  $\zeta_n$  and the molecular fragment  $\phi_n$ , we revert to Cartesian coordinate space for a moment and remove mass coupling by simply assuming that all masses but the ones which belong to the atoms of fragment  $\phi_n$  are zero. With this assumption, the equations of motion (6) will lead to a pure internal vibration of fragment  $\phi_n$ . Of course, such an internal vibration is of little use for a chemist, who prefers to think in terms of internal coordinates (more generally, internal parameters) rather than Cartesian coordinates. However, since  $m_i = 0$  ( $i \in \phi_m$ ) implies that the generalized momentum  $p_i = 0$ , one can extend the assumption of all atoms not belonging to  $\phi_n$  as being massless points just describing the molecular geometry and apply it to internal parameters by assuming that all internal parameters  $\zeta_m$  ( $m \neq n$ ) are associated with the generalized momentum  $p_m = 0$ . With this assumption, the Euler-Lagrange Eqs. (19) take the form of (23) and (24):

$$p_n = \frac{\partial L(\boldsymbol{\zeta}, \dot{\boldsymbol{\zeta}})}{\partial \dot{\zeta}_n} \neq 0 \quad (23a)$$

$$p_m = \frac{\partial L(\boldsymbol{\zeta}, \dot{\boldsymbol{\zeta}})}{\partial \dot{\zeta}_m} = 0 \quad \forall m, m \neq n \quad (23b)$$

$$\dot{p}_n = \frac{\partial V}{\partial \zeta_n} \quad (24a)$$

$$\dot{p}_m = \frac{\partial V}{\partial \zeta_m} = 0 \quad \forall m \neq n. \quad (24b)$$

Equations (24) can be solved by adding Eq. (25):

$$\dot{p}_n = \lambda \quad (25a)$$

$$\lambda = \frac{\partial V}{\partial \zeta_n}. \quad (25b)$$

Equations (24b) and (25b) are used to express all internal parameters  $\zeta$  as functions of  $\lambda$ :

$$\begin{aligned} \zeta_1 &= \zeta_1(\lambda) \\ &\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ \zeta_N &= \zeta_N(\lambda) \end{aligned} \quad (26)$$

Equation (27) determines the form of internal vibrations  $\mathbf{v}_n$  because it defines one-dimensional subspaces within the full configuration space. The motion in a one-dimensional subspace can be described by vector  $\mathbf{v}_n$ , which can be found by linearization (e.g., via a Taylor expansion at point  $\lambda = 0$ ) of Eq. (26). If needed, the time dependence of  $\lambda$  can be found using generalized momenta

$$p_n = p_n(\boldsymbol{\zeta}, \dot{\boldsymbol{\zeta}}) = p_n(\boldsymbol{\lambda}, \dot{\boldsymbol{\lambda}}) \quad (27)$$

in connection with Equations (25a) and (26). In this way, one obtains an internal vibration  $\mathbf{v}_n = \mathbf{a}_n$  for parameter  $\zeta_n$  associated with fragment  $\phi_n$ .

A set of equations similar to (25) can be obtained by applying a completely different approach. One can displace parameter  $\zeta_n$  from its equilibrium value ( $\zeta_n = 0$ ) and keep it frozen and equal to a constant  $\zeta_n^*$ . At the same time, all other coordinates can relax until the molecular energy attains its minimum. Hence, parameter  $\zeta_n^*$  leads the corresponding motion as described in Eq. (4) (*leading parameter principle*). For obvious reasons, one can call the vibrations generated by  $\zeta_n^*$  adiabatic vibrations defined by (28):

$$V(\boldsymbol{\zeta}) = \min \quad (28a)$$

$$\zeta_n = \text{const} = \zeta_n^*. \quad (28b)$$

Equation (28) can easily be solved using the method of Lagrange multipliers:

$$\frac{\partial}{\partial \zeta_m} [V(\boldsymbol{\zeta}) - \lambda(\zeta_n - \zeta_n^*)] = 0 \quad m = 1, \dots, N. \quad (29)$$

This leads to Eqs. (30):

$$\lambda = \frac{\partial V}{\partial \zeta_n} \quad (30a)$$

$$0 = \frac{\partial V}{\partial \zeta_m} \quad \forall m, m \neq n, \quad (30b)$$

which are identical to Eqs. (24b) and (25b). Hence, the approximation based on the *massless internal parameters*  $\zeta_m$  is equivalent to the adiabatic approximation.

## Adiabatic Principle Applied to the Harmonic Approximation

Assuming that the vibrational problem has been solved in the harmonic approximation, the potential energy and each internal parameter  $\zeta_n$  can be expressed as functions of  $N_{vib}$  normal mode coordinates  $Q_\mu$  [1-6]:

$$V(\mathbf{Q}) = \frac{1}{2} \sum_{\mu=1}^{N_{vib}} k_\mu Q_\mu^2 \quad (31)$$

$$\zeta_n(\mathbf{Q}) = \sum_{\mu=1}^{N_{vib}} D_{n\mu} Q_\mu, \quad (32)$$

where matrix  $\mathbf{D}$  collects in its columns vectors  $\mathbf{d}_\mu$ . Inserting (31) into (28) and using the method of Lagrange multipliers, one obtains

$$\frac{\partial}{\partial Q_\mu} [V(\mathbf{Q}) - \lambda(\zeta_n(\mathbf{Q}) - \zeta_n^*)] = 0 \quad (33)$$

and

$$Q_\mu^{(n)} = \frac{D_{n\mu}}{k_\mu} \lambda. \quad (34)$$

The superscript  $n$  denotes the solution for internal parameter  $\zeta_n$ , where

$$\zeta_n(\mathbf{Q}) = \zeta_n^* \quad (35)$$

as described above. Using Eqs. (32), (34), and (35),  $\lambda$  can be found as a function of  $\zeta_n^*$ :

$$\lambda = \frac{1}{\sum_{\mu=1}^{N_{vib}} \frac{D_{n\mu}^2}{k_\mu}} \zeta_n^*. \quad (36)$$

By inserting Eq. (36) into Eq. (34), one obtains the normal coordinates as a function of  $\zeta_n^*$ :

$$Q_\mu^{(n)} = Q_{\mu n}^0 \zeta_n^*, \quad (37)$$

where  $Q_{\mu n}^0$  is a constant defined as

$$Q_{\mu n}^0 = \frac{\frac{D_{n\mu}}{k_\mu}}{\sum_{\nu=1}^{N_{vib}} \frac{D_{n\nu}^2}{k_\nu}}. \quad (38)$$

According to Eq. (37), any change in parameter  $\zeta_n^*$  leads to a movement of all normal coordinates along adiabatic vector  $\mathbf{a}_n$ , the components of which in normal coordinate space are given by

$$(\mathbf{a}_n)_\mu = Q_{\mu n}^0. \quad (39)$$

In view of Eq. (39), it is straightforward to transform adiabatic vectors into the space of Cartesian displacements:

$$(\mathbf{a}_n)_i = \sum_{\mu=1}^{N_{vib}} l_{i\mu} (\mathbf{a}_n)_\mu \quad i = 1, \dots, 3K, \quad (40)$$

where  $l_{i\mu}$  is a component of the normal mode  $\mathbf{l}_\mu$  defined in Eq. (22).

## Definition of Internal Force Constant $k_n$ , Internal Mass $m_n$ , and Internal Frequency $\omega_n$

Once the vector  $\mathbf{v}_n$ , which determines the movement of the molecule under the influence of parameter  $\zeta_n^*$ , is known, one can define a force constant, which corresponds to such a motion, by inserting (4) into the expression for the potential energy of the molecule in the harmonic approximation [see Eq. (8)]:

$$V(\zeta_n^*) = \frac{1}{2} k_n \zeta_n^{*2}, \quad (41)$$

where the internal force constant  $k_n$  is given by

$$k_n = \mathbf{v}_n^+ \mathbf{f}_{\mathbf{v}_n}. \quad (42)$$

A typical mass  $M_n$  associated with the internal vibration  $\mathbf{v}_n$  could be defined by inserting Eq. (4) into the expression for the kinetic energy  $T(\dot{\mathbf{x}})$  [see Eq. (7)]:

$$T(\dot{\zeta}_n^*) = \frac{1}{2} M_n \dot{\zeta}_n^{*2}, \quad (43)$$

where the internal mass  $M_n$  is given by

$$M_n = \mathbf{v}_n^+ \mathbf{M} \mathbf{v}_n. \quad (44)$$

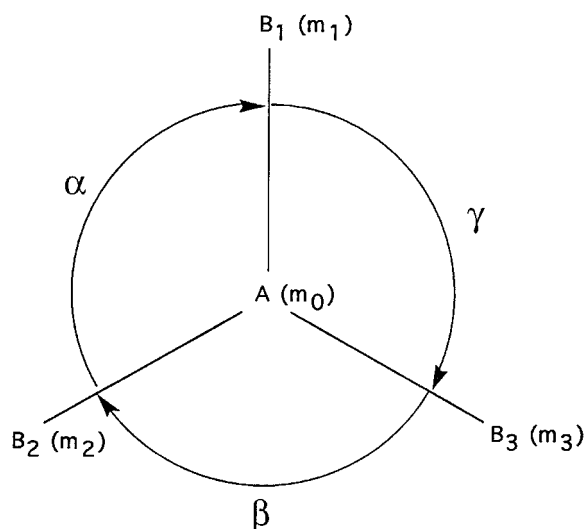
From (42) and (44), one obtains the characteristic fragment frequency  $\Omega_n$ :

$$\Omega_n^2 = \frac{k_n}{M_n}, \quad (45)$$

where  $\Omega$  rather than  $\omega$  is used to indicate that, according to (44) and (45), all masses of a molecule are considered in the definition of  $\Omega$ . Although  $\Omega_n$  was derived from a rigorous dynamical principle, its definition is problematic because the value of the internal frequency  $\Omega_n$  becomes sensitive to the environment of molecular fragment  $\phi_n$  which can lead to unphysical shifts of internal frequencies as will be shown in article II [14].

Therefore, one has to proceed in a different way to find a typical mass  $m_n$  that opposes any change in the internal parameter  $\zeta_n$ . One possibility is to delete masses in the full mass matrix  $\mathbf{M}$  that do not contribute to parameter  $\zeta_n$ . In this way, a new mass  $M_n^0$  is obtained that can be used to calculate an intrinsic frequency  $\Omega_n^0$  with Eq. (45). For example, one could keep only the two masses connected with a bond-stretching motion or the three masses associated with a bending motion. It can easily be shown that, provided the bond does not rotate or translate,  $M_n^0$  is exactly equal to the reduced mass of the bond.

But this procedure will become questionable if more complicated parameters such as symmetry-adapted linear combinations of internal parameters are studied. For example, the bending motion of a planar molecule  $AB_3$  can be described by the angle combination  $\alpha + \beta$  associated with masses



**FIGURE 1.** Internal coordinates of an  $AB_3$  molecule with nuclei  $A$ ,  $B_1$ ,  $B_2$ , and  $B_3$  and the nuclear masses  $m_0$ ,  $m_1$ ,  $m_2$ , and  $m_3$ , respectively.

$m_0$ ,  $m_1$ ,  $m_2$ , and  $m_3$  (see Fig. 1). Because of the planarity of the molecule, it holds that

$$\Delta\gamma = -\Delta(\alpha + \beta), \quad (46)$$

where  $\gamma$  is associated with masses  $m_0$ ,  $m_1$ , and  $m_3$ , leaving out mass  $m_2$ . Hence,  $M_n^0$  can be defined in two different ways, leading to two different  $\Omega_n^0$  values, although both  $\alpha + \beta$  and  $\gamma$  are associated with one and the same internal bending frequency. While in Cartesian space it is always clear which set of coordinates belongs to which mass, in internal coordinate space, it is not always clear how to select all masses that might belong to a given internal parameter  $\zeta_n$ .

Clearly, one has to find a more direct way of defining the internal mass  $m_n$  associated with the internal parameter  $\zeta_n$ . Two conditions should be fulfilled in this connection. First, the mass  $m_n$  should be extractable from the functional form of the internal parameter  $\zeta_n$ . Second,  $m_n$  should directly be connected to the vibrational motion  $\mathbf{v}_n$  caused by a change in  $\zeta_n$ .

To fulfill these two conditions, one has to ask how the atoms of the molecule have to move so that the kinetic energy adopts a minimum and the generalized velocity  $\dot{\zeta}_n$  becomes identical with  $\dot{\zeta}_n^*$ , i.e., the system fulfills Eqs. (47) and (48):

$$T(\dot{\mathbf{x}}) = \frac{1}{2}\dot{\mathbf{x}}^+ \mathbf{M} \dot{\mathbf{x}} = \min \quad (47)$$

$$\mathbf{b}_n^+ \dot{\mathbf{x}} = \mathbf{b}_n^+ \mathbf{v}_n \dot{\zeta}_n^*, \quad (48)$$

where vector  $\mathbf{b}_n$  corresponds to the  $n$ th column of the  $\mathbf{B}$  matrix [1-6] and  $\mathbf{b}_n^+ \mathbf{v}_n \dot{\zeta}_n^*$  is the generalized velocity of parameter  $\zeta_n$  when the system moves according to (4). Using the Lagrange multiplier  $\lambda$  and combining (47) and (48), one obtains

$$\frac{\partial}{\partial \dot{x}_i} \left( \frac{1}{2} \dot{\mathbf{x}}^+ \mathbf{M} \dot{\mathbf{x}} - \lambda (\mathbf{b}_n^+ \dot{\mathbf{x}} - \mathbf{b}_n^+ \mathbf{v}_n \dot{\zeta}_n^*) \right) = 0 \quad (49)$$

and

$$\dot{\mathbf{x}} = \mathbf{M}^{-1} \mathbf{b}_n \lambda. \quad (50)$$

By inserting Eq. (50) into (48), the Lagrange multiplier  $\lambda$  is given by (51):

$$\lambda = \frac{\mathbf{b}_n^+ \mathbf{v}_n}{\mathbf{b}_n^+ \mathbf{M}^{-1} \mathbf{b}_n} \dot{\zeta}_n^*. \quad (51)$$

With Eq. (51),  $\dot{\mathbf{x}}$  of (50) can be determined as a function of  $\dot{\zeta}_n^*$ . In turn, the kinetic energy of (47) can be written according to (52):

$$T(\dot{\zeta}_n^*) = \frac{1}{2} m_n \dot{\zeta}_n^{*2}, \quad (52)$$

with the internal mass  $m_n$  associated with parameter  $\zeta_n$  being given by

$$m_n = \frac{(\mathbf{b}_n^+ \mathbf{v}_n)^2}{\mathbf{b}_n^+ \mathbf{M}^{-1} \mathbf{b}_n}. \quad (53)$$

The denominator of Eq. (53) can be recognized as element  $G_{nn}$  of the  $\mathbf{G}$  matrix.

Once the internal force constant  $k_n$  [see Eq. (42)] and the internal mass  $m_n$  [see Eq. (53)] have been derived, the internal frequency  $\omega_n$  is given by Eq. (54):

$$\omega_n^2 = \frac{\mathbf{v}_n^+ \mathbf{f} \mathbf{v}_n}{(\mathbf{b}_n^+ \mathbf{v}_n)^2 \frac{1}{G_{nn}}}. \quad (54)$$

From Eq. (54), two important conclusions can be drawn:

1. If parameter  $\zeta_n$  represents the change in the bond distance of a diatomic molecular fragment  $AB$  caused by  $AB$  bond stretching, then  $1/G_{nn}$  will be exactly equal to the reduced mass defined by  $m_A m_B / (m_A + m_B)$ . Equation (54) reveals that, in the general case,  $1/G_{nn}$  can be taken as the reduced mass associated with internal parameter  $\zeta_n$ , no matter which functional form  $\zeta_n$  takes.
2. Term  $(\mathbf{b}_n^+ \mathbf{v}_n)^2$  in the denominator of (54) guarantees proper normalization of vector  $\mathbf{v}_n$ . It suggests that the force constant  $k_n$  should be calculated according to (55) rather than (42):

$$k_n = \mathbf{v}_n'^+ \mathbf{f} \mathbf{v}_n', \quad (55)$$

with  $\mathbf{v}_n'$  given by

$$\mathbf{v}_n' = \frac{\mathbf{v}_n}{\mathbf{b}_n^+ \mathbf{v}_n}. \quad (56)$$

This means that in Eq. (4)  $\mathbf{v}_n'$  is used rather than  $\mathbf{v}_n$ :

$$\mathbf{x}^* = \mathbf{v}_n' \zeta_n^*. \quad (57)$$

If Eq. (57) is multiplied from the left by  $\mathbf{b}_n^+$ , then one will obtain  $\zeta_n = (\mathbf{b}_n^+ \mathbf{v}_n') \zeta_n^*$ . Because of Eq. (56),  $\mathbf{b}_n^+ \mathbf{v}_n' = 1$ , which ensures that  $\zeta_n$  and  $\zeta_n^*$  are the same during an internal vibration. This is of crucial importance for the calculation of internal force constants. Note that if  $\mathbf{v}_n = \mathbf{a}_n$ ,  $\mathbf{v}_n$  will be properly normalized in the sense that  $\mathbf{b}_n^+ \mathbf{a}_n = 1$ . The term  $(\mathbf{b}_n^+ \mathbf{v}_n)^2$  in the denominator of (54) is only important when  $\zeta_n$  is not equal to  $\zeta_n^*$ . This is the case for choosing  $\mathbf{c}$ -vectors calculated with redundant sets of parameters as internal modes as will be discussed in the following article [14].

## Summary and Conclusions

One of the major goals of vibrational spectroscopy is to associate measured frequencies with structural features of a molecule and, thereby, to facilitate its identification. These efforts have led to a number of rules that concern the similarity and transferability of force constants and frequencies from one molecule to the other provided that they contain similar structural units [1–9]. To provide a mathematical basis for the comparison of measured vibrational frequencies and force constants, we have formulated the *leading parameter principle* [Eq. (8)] which enables one to investigate molecular fragments in terms of their internal vibrations defined by the pair  $(\zeta_n, \mathbf{v}_n)$ .

We have discussed adiabatic vectors  $\mathbf{a}_n$  as a unique choice for internal vibrational mode vectors  $\mathbf{v}_n$ . The derivation of the adiabatic vectors has been motivated by the observation that the masses of the atoms of a molecule effectively hinder the appearance of pure internal vibrations  $\mathbf{v}_n$  associated with fragment  $\phi_n$ . However, localized internal vibrations  $\mathbf{v}_n$  can be obtained by setting the generalized momenta associated with those internal parameters not used for the description of fragment  $\phi_n$  to zero and solving the Euler–Lagrange equations under this condition. This approach is equivalent to exciting the internal motion  $\mathbf{v}_n$  by a constant perturbation  $\zeta_n^*$  of the leading parameter associated with  $\phi_n$  and, then, relaxing the distortions of all other internal coordinates  $q_m$  until a minimum of the energy is obtained.

Once adiabatic internal vibrations are defined, there are several choices for the definition of an adiabatic internal vibrational frequency. We have considered the three internal frequencies  $\Omega_n, \Omega_n^0,$



and  $\omega_n$  that possess the following properties:

1. Frequency  $\Omega_n$  depends on all atomic masses of a molecule and, therefore,  $\Omega_n$  is unlikely to be a proper choice for an internal, fragment characteristic frequency.
2. Frequency  $\Omega_n^0$  depends on just those masses associated with the internal parameter  $\zeta_n$  and, therefore, should be a better choice for a fragment frequency. However, the definition of  $\Omega_n^0$  is not clear in the general case.
3. Frequency  $\omega_n$  is directly derived from the properties of the internal quantities ( $\zeta_n, \mathbf{v}_n$ ) by minimizing the kinetic energy under the constraint that the generalized velocity of the internal parameter  $\zeta_n$  becomes identical with that of the leading parameter  $\zeta_n^*$ . In this way, an internal mass  $m_n$  is defined that directly leads to the frequency  $\omega_n$  of Eq. (54) as the best choice for an internal frequency.

The choice of  $m_n$  as an appropriate fragment mass is confirmed by the fact that it represents a generalized reduced mass  $1/G_{nn}$ . Furthermore, it guarantees that fragment frequencies do not depend on the masses of those atoms that do not belong to  $\phi_n$  and, therefore are typical of  $\phi_n$  and its properties. Using the internal mass  $m_n$  and the internal frequency  $\omega_n$ , it is straightforward to calculate a characteristic internal force constant  $k_n$  [Eq. (55)] associated with parameter  $\zeta_n$  and fragment  $\phi_n$ . In this way, the molecular fragment  $\phi_n$  is characterized by the internal frequency  $\omega_n$ , the internal mass  $m_n$ , and the internal force constant  $k_n$  in a unique way, which allows the comparison of different molecular fragments.

There are immediately a number of applications of adiabatic internal modes that lead to a new dimension in the analysis of vibrational spectra. For example, the adiabatic vectors  $\mathbf{a}_n$  defined in this work are perfectly suited to present a set of localized internal modes that can be used to analyze delocalized normal modes. In the following articles, we will investigate this possibility [14–16].

## ACKNOWLEDGMENTS

This work was supported by the Swedish Natural Science Research Council (NFR). All calculations were done on the CRAY YMP/416 of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden. The authors thank the NSC for a generous allotment of computer time.

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