

A New Way of Analyzing Vibrational Spectra. III. Characterization of Normal Vibrational Modes in Terms of Internal Vibrational Modes

ZORAN KONKOLI, DIETER CREMER

Department of Theoretical Chemistry, University of Göteborg Kemigården 3, S-41296 Göteborg, Sweden

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

ABSTRACT: The concept of characterizing normal vibrational modes \mathbf{l}_μ in terms of internal vibrational modes \mathbf{v}_n typical of molecular fragments or structural subunits is developed. Essential for this concept is the amplitude $\mathcal{A}_{n\mu}$ that provides the basis for a quantitative comparison of modes \mathbf{l}_μ and \mathbf{v}_n and, by this, facilitates the extraction of chemical information out of vibrational spectra. Twelve possibilities of defining amplitude \mathcal{A} are tested with regard to (a) the physical basis of the definition of \mathcal{A} , (b) the dependence of \mathcal{A} on the set of internal parameters chosen to describe the molecule, and (c) the amount of chemical information transferred by \mathcal{A} . The two most promising candidates for a generally applicable amplitude \mathcal{A} are based on adiabatic internal modes and a comparison of \mathbf{l}_μ and \mathbf{v}_n with the help of mass or force constant matrix. For the practical testing of amplitude \mathcal{A} , three different criteria are developed. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* 67: 29–40, 1998

Introduction

In vibrational spectroscopy, one measures the infrared or Raman spectra of vibrating molecules. From the spectra, the vibrational frequencies ν_μ^{exp} are obtained by determining the

positions of maximum intensity of the vibrational bands. Utilizing previous measurements that have led to the identification of structure-specific frequencies ν_n , one determines whether measured vibrational frequencies ν_μ^{exp} can be related to frequencies of structural units such as CC double bonds and keto groups [1]. If in a particular case a sufficiently large number of identifications have been made, it will be possible to verify or identify the structure of a molecule with the help of vibrational spectroscopy. This procedure is schemati-

Correspondence to: D. Cremer.

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

cally indicated in the sequence (1)–(4) of Figure 1. If this sequence is closed to a circle, the vibrational spectrum and molecular structure can be related in the sense that it is not only possible to determine the structure of a molecule with the help of measured vibrational spectra but also to predict the vibrational spectra of a given molecule once its structure is known [i.e., predicting (1) on the basis of (4) in Fig. 1].

While Figure 1 describes the ideal case, the practice of vibrational spectroscopy is far from identifying the exact structure of any molecule by analysis of its vibrational spectra. Problems arise

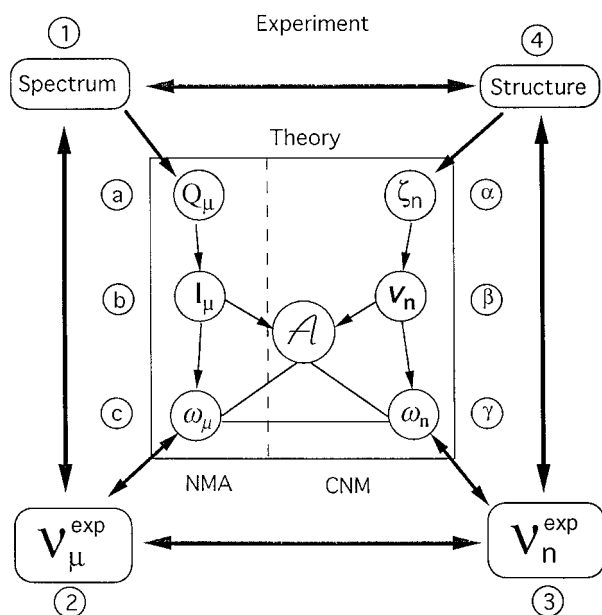


FIGURE 1. Comparison of experimental (outer circle) and theoretical vibrational spectroscopy (inner circle). In the experiment, a vibrational spectrum of a molecule is measured (1), normal mode frequencies ν_{μ}^{exp} are determined (2) and analyzed to identify characteristic fragment frequencies ν_n^{exp} (3) that can be associated with structural units so that the structure of the molecule can be unravelled (4). In the theoretical part of vibrational spectroscopy, the normal mode analysis (NMA) is carried out, which leads to normal mode coordinates Q_{μ} (a), normal mode vibrations I_{μ} (b), and normal mode frequencies ω_{μ} (c, left side of inner circle). The NMA is complemented by the characterization of normal mode (CNM) analysis, which connects internal parameters ζ_n describing the structural units of a molecule (α) with the internal vibrational modes v_n (β) and the characteristic fragment frequencies ω_n (γ , right side of inner circle). NMA and CNM are linked by the amplitude \mathcal{A} , which provides the basis for the comparison of internal vibrational modes v_n with normal vibrational modes I_{μ} .

from the extraction of fragment-specific frequencies ν_n , which can be used to verify all structural units as well as their connections within a molecule. Certainly, there have been many accomplishments to assign typical frequencies ν_{μ}^{exp} to molecular fragments ϕ_n [1]; however, in none of these cases was it possible to generalize assignments to any arbitrary molecular unit and to get in this way a building-block principle for molecules and their vibrational spectra.

In this situation, theory in general, but in particular ab initio theory, provides important additional information. First, it is possible to calculate IR and Raman spectra in the harmonic approximation (leading to ω_{μ} rather than ν_{μ}) with satisfactory accuracy in a routine manner. Automatically, the normal modes I_{μ} of the vibrating molecule are characterized in terms of normal coordinates Q_{μ} and normal frequencies ω_{μ} as is indicated in Figure 1 by the sequence (a–c), which presents the basis for the normal mode analysis (NMA). Calculated frequencies ω_{μ} can be compared with measured frequencies (relating step c and step 2 in Fig. 1) and, in this way, facilitate the identification of an unknown compound since agreement of measured and calculated frequencies suggests that the geometry used in the calculation represents the geometry of the molecule investigated by vibrational spectroscopy.

Apart from this, theory provides a second possibility of structure determination with the help of vibrational spectroscopy, which has not been used so far, but may represent the key to the problem of relating structure and vibrational spectra. By theoretical means, one can determine elementary modes of suitable structural units or molecular fragments ϕ_n that are associated with internal coordinates q_n describing these fragments. Such modes we have called internal modes [2, 3] since they play the same role in the understanding of the vibrating molecule as internal coordinates play in the understanding of molecular geometry and conformation, i.e., internal modes add a dynamic part to the static description of molecules with the help of internal coordinates.

The internal modes, each of which is localized in a different molecular fragment, present the basis for characterizing normal modes (CNM analysis). For this purpose, one has to define an amplitude $\mathcal{A}_{n\mu}$, which specifies the contribution of a particular internal mode v_n to a given delocalized normal mode I_{μ} . Utilizing amplitudes $\mathcal{A}_{n\mu}$, one can de-

compose normal modes in terms of internal modes and, in this way, exactly relate the normal modes of a molecule to its structural units. This clearly facilitates the use of vibrational spectroscopy as a structure-determining tool and enriches its possible uses within chemistry.

Clearly, the assets of a useful, in itself noncontradictory, and physically based CNM analysis are the internal vibrational motions as well as the amplitudes \mathcal{A} that relate internal modes to normal modes. We presented in the first article of this series, henceforth called article I [2], *adiabatic internal modes* \mathbf{a}_n as the appropriate candidates for internal modes and compared their properties with those of c-vector internal modes in article II of this series [3]. In this work, we focused on the possibilities of decomposing normal modes into internal modes using amplitudes \mathcal{A} . For this purpose, we suggest appropriate definitions of \mathcal{A} and also investigate the so-called density matrix \mathbf{P} , which is used within the potential energy distribution (PED) analysis to characterize normal modes [4–7]. Each amplitude will be tested with the help of appropriate criteria that guarantee a physically reasonable basis of the CNM analysis.

Description of Normal Modes with the Help of Amplitudes \mathcal{A}

There are no explicit criteria that help to define a suitable amplitude \mathcal{A} needed to describe the contribution of internal modes to normal modes and, then, to judge on the quality of this definition. However, there are properties that are implicitly assumed to be associated with amplitudes \mathcal{A} . These can be formulated in the following way:

1. Symmetry-equivalent internal modes associated with symmetry-equivalent internal parameters must have the same amplitudes in the case that the normal mode being decomposed is symmetric (*symmetry criterion*).
2. The results of the CNM analysis should not change significantly if some internal motions with low amplitudes are changed or deleted in the expansion of the normal modes as might happen when changing a redundant set of internal parameters into another set (*stability of results*).
3. Since it is not possible to directly evaluate the quality of a given definition of $\mathcal{A}_{n\mu}$, one

has to do this in an indirect way by comparing a normal mode frequency with suitable reference frequencies associated with internal parameters ζ_n .^{*} It is physically reasonable to expect that if all normal modes \mathbf{l}_μ are studied for fixed internal modes \mathbf{v}_n (associated with fixed parameters ζ_n), then the magnitude of amplitudes $\mathcal{A}_{n\mu}$ should become the smaller the larger the difference $\Delta\omega_{n\mu}$ between the normal mode frequency ω_μ and the fixed reference frequency ω_n is. If this is the case, one can say that the dynamical origin of the normal mode principle will be fulfilled. In Appendix A, a general correlation pattern for $\mathcal{A}_{n\mu}$ vs. $\Delta\omega_{n\mu}$ is derived (*dynamical origin of normal mode concept*).

Provided that the dynamical origin of the normal mode concept is correctly considered, the amplitude $\mathcal{A}_{n\mu}$ will adopt a large value if the frequency difference $\Delta\omega_{\mu n} = \omega_\mu - \omega_n$ is relatively small, which simply means that the internal mode \mathbf{v}_n associated with the internal parameter ζ_n dominates the normal mode \mathbf{l}_μ and that the normal mode frequency ω_μ indicates the presence of the structural unit ϕ_n characterized by ζ_n and the internal mode frequency ω_μ :

$$\mathcal{A}_{n\mu}(\text{large}) \Rightarrow \Delta\omega_{\mu,n}(\text{small}). \quad (1)$$

Relationship (1) is the basis for the empirical assignment of measured frequencies to structural units or fragments of a molecule.

Similarly, if there is a normal mode frequency ω_ν placed far from an internal mode frequency ω_n associated with fragment ϕ_n , then one will not expect a large amplitude since it is unlikely that the internal mode \mathbf{v}_n dominates the normal mode \mathbf{l}_μ :

$$\Delta\omega_{\mu,n}(\text{large}) \Rightarrow \mathcal{A}_{n\mu}(\text{small}). \quad (2)$$

Hence, the case

$$\Delta\omega_{\mu,n}(\text{large}) \Rightarrow \mathcal{A}_{n\mu}(\text{large}) \quad (3)$$

should not occur. Of course, due to strong couplings within the molecule, it can happen that although a normal mode frequency ω_μ possesses a similar value as that of the internal mode fre-

^{*} We prefer to use the term internal parameter rather than internal coordinate since the former covers all possible choices of a coordinate (puckering coordinates, natural coordinates, delocalized coordinates, etc.)

quency ω_n , normal mode \mathbf{I}_μ has nothing in common with internal mode \mathbf{v}_n . This will be indicated by a low value of amplitude $\mathcal{A}_{n\mu}$ according to

$$\Delta\omega_{\mu,n}(\text{small}) \text{ and } \mathcal{A}_{n\mu}(\text{small}). \quad (4)$$

If amplitudes $\mathcal{A}_{n\mu}$ are plotted as a function of $\Delta\omega_{\mu,n}$, then the distribution of amplitude points should be enveloped by a Lorentzian (bell-shaped) curve (Fig. 2) similar to the one describing the line shape of spectroscopic bands [8], since this curve complies with expectations (1)–(4).

Definition of Internal Mode Amplitudes \mathcal{A}

Any procedure to define an amplitude \mathcal{A} must guarantee that normal and internal vibrational modes are related in a physically reasonable way. The change in an internal parameter ζ_n of a molecule is associated with the vibrational mode \mathbf{v}_n of that structural unit ϕ_n that is described by ζ_n [2]. The vector \mathbf{v}_n describes how the molecule vibrates when parameter ζ_n that initiates (“leads”) the internal motion is slightly distorted from its equilibrium value. From the NMA, one obtains normal mode vectors \mathbf{I}_μ , each of which shows how the atoms of a molecule move when the normal coordinate Q_μ is changed. By comparing the normal mode \mathbf{I}_μ with the internal mode \mathbf{v}_n , the amplitude $\mathcal{A}_{n\mu}$ is obtained that describes \mathbf{I}_μ in terms of

the vibration of the smaller structural unit ϕ_n represented by displacement vector \mathbf{v}_n . Clearly, amplitude $\mathcal{A}_{n\mu}$ has to be defined as a function of \mathbf{I}_μ and \mathbf{v}_n :

$$\mathcal{A}_{n\mu} = f(\mathbf{I}_\mu, \mathbf{v}_n). \quad (5)$$

In this article, we consider two choices for the internal mode vector \mathbf{v}_n , namely, \mathbf{v}_n equal to the adiabatic internal mode vector \mathbf{a}_n (see article I [2]) and \mathbf{v}_n equal to the vector \mathbf{c}_n where the \mathbf{c} -vectors of matrix \mathbf{C} describe the transformation from Cartesian to internal coordinates [9, 10]. The choice $\mathbf{v}_n = \mathbf{c}_n$ is implicitly assumed within the PED analysis [4–7] (see also article II [3]). As has been shown in articles I [2] and II [3], adiabatic vectors \mathbf{a}_n have a better physical justification than do vectors \mathbf{c}_n , which should pay off when defining the amplitude $\mathcal{A}_{n\mu}$. However, a priori, one cannot guarantee that this pays off when defining and using amplitudes for the CNM analysis and, therefore, explicit consideration of the PED analysis both from a theoretical and a practical point of view is needed.

Once \mathbf{v}_n is chosen, one can compare the normal mode vibration \mathbf{I}_μ with the vibration \mathbf{v}_n of a structural unit ϕ_n by calculating the scalar product $(\mathbf{I}_\mu, \mathbf{v}_n)$. We define $\mathcal{A}_{n\mu}$ as

$$A_{n\mu} = \frac{(\mathbf{I}_\mu, \mathbf{v}_n)^2}{(\mathbf{v}_n, \mathbf{v}_n)(\mathbf{I}_\mu, \mathbf{I}_\mu)}, \quad (6)$$

where we use symbol $A_{n\mu}$ to distinguish between a specific definition of \mathcal{A} and the general amplitude $\mathcal{A}_{n\mu}$. The denominator in (6) accounts for proper normalization and guarantees that $A_{n\mu}$ will adopt values between 0 and 1.

AMPLITUDES DERIVED FROM A DENSITY MATRIX P

In the PED analysis [4–7], one defines a density matrix P_{nm}^μ that describes normal mode μ in terms of vibrations represented by vectors \mathbf{v}_n . By expanding \mathbf{I}_μ in terms of vectors \mathbf{v}_n according to Eq. (7),

$$\mathbf{I}_\mu = \sum_n \mathbf{v}_n t_{n\mu}, \quad (7)$$

and expressing the scalar product $(\mathbf{I}_\mu, \mathbf{I}_\mu)$ according to Eq. (8),

$$(\mathbf{I}_\mu, \mathbf{I}_\mu) = \sum_{n,m} t_{n\mu} t_{m\mu} (\mathbf{v}_n, \mathbf{v}_m), \quad (8)$$

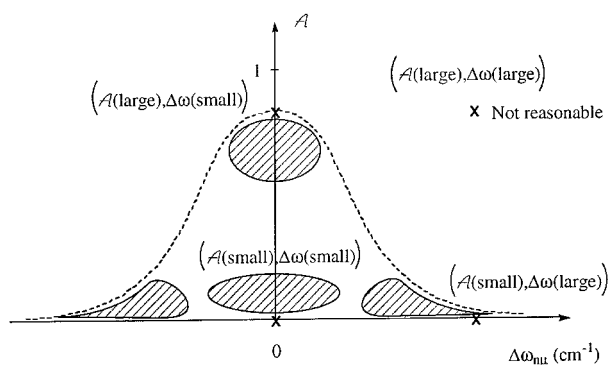


FIGURE 2. Different possibilities that can occur when plotting amplitudes $\mathcal{A}_{n\mu}$ in dependence of the difference $\Delta\omega_{\mu,n}$, between normal mode frequencies ω_μ and characteristic fragment frequencies ω_n . The dashed line indicates the enveloping Lorentzian (bell-shaped) curve that can be expected in the case of a physically well-defined amplitude (see text).

one obtains the general definition of the \mathbf{P} matrix elements by dividing Eq. (8) by $(\mathbf{1}_\mu, \mathbf{1}_\mu)$:

$$1 = \sum_{n,m} P_{nm}^\mu, \quad (9)$$

with

$$P_{nm}^\mu = \frac{t_{n\mu} t_{m\mu} (\mathbf{v}_n, \mathbf{v}_m)}{(\mathbf{1}_\mu, \mathbf{1}_\mu)}. \quad (10)$$

Clearly, elements of the \mathbf{P} matrix can fulfill the role of amplitudes used in the CNM approach.

There is only one situation in which A -type and P -type amplitudes lead to identical descriptions of normal modes in terms of internal modes, namely, that in which a set of orthogonal vectors \mathbf{v}_n is chosen in the sense that

$$(\mathbf{v}_n, \mathbf{v}_m) = \delta_{n,m} (\mathbf{v}_n, \mathbf{v}_n), \quad (11)$$

and, accordingly, $A_{n\mu} = P_{nn}^\mu$. However, generally, internal modes \mathbf{v}_n are not orthogonal and, therefore, A - and P -type amplitudes lead to different decompositions of normal modes $\mathbf{1}_\mu$. From the definition of A amplitudes [Eq. (6)], it is obvious that $A_{n\mu}$ does not depend on how the other internal parameters ζ_m ($m \neq n$) not associated with vector \mathbf{v}_n are chosen. As long as $A_{n\mu}$ is considered for the same \mathbf{v}_n and ζ_n , the overall choice of the set of internal parameters does not effect the value of the amplitude $A_{n\mu}$. This is of advantage for a chemically oriented analysis of normal modes: For example, if the contribution of one particular internal mode associated with the structural unit ϕ_n and the internal parameter ζ_n (e.g., a C=C bond and its associated length) to the N normal modes of a molecule is of interest, the different values of $A_{n\mu}$ with $\mu = 1, \dots, N_{vib}$ ($N_{vib} = 3K - L$: number of vibrations; K : number of atoms; L : number of translations and rotations) can be calculated and compared without any need to define the other internal parameters of the molecule.

Contrary to A -type amplitudes, P -type amplitudes are parameter set dependent since the overall choice of parameters ζ_m , $m \neq n$ determines the value of P_{nm}^μ given in Eq. (10). This is confirmed in practice, which reveals that P -type amplitudes are very sensitive to the choice of the parameter set, which, in any case, has to be complete [11] to obtain a useful P_{nm}^μ value [12].

DEFINITION OF SCALAR PRODUCTS

The scalar product (\mathbf{a}, \mathbf{b}) , which appears in the definition of both the amplitude $A_{n\mu}$ [Eq. (6)] and the density matrix P_{nm}^μ (10), can be defined in the most general way as

$$(\mathbf{a}, \mathbf{b}) = \sum_{i,j} a_i O_{ij} b_j, \quad (12)$$

where O_{ij} is an element of the metric matrix \mathbf{O} and a_i and b_j are components of vectors \mathbf{a} and \mathbf{b} in Cartesian space. For the metric \mathbf{O} , there are three natural choices, namely,

$$\begin{aligned} \text{(a)} \quad O_{ij} &= \delta_{ij} \\ \text{(b)} \quad O_{ij} &= M_{ij} \\ \text{(c)} \quad O_{ij} &= f_{ij}, \end{aligned} \quad (13)$$

with M_{ij} and f_{ij} being elements of the mass and force constant matrix, respectively. Equation (13a) provides an estimate whether the two vectors \mathbf{a} and \mathbf{b} are spatially close, i.e., it measures their "spatial overlap". Equation (13b) compares the two vectors kinetically ("mass comparison") and Eq. (13c) compares them dynamically ("force comparison"). Equations (13b) and (13c) reveal the influence of the atomic masses (via mass matrix \mathbf{M}) or that of the electronic structure (via force constant matrix \mathbf{f}) on the form of the normal mode $\mathbf{1}_\mu$. This is discussed in more detail in Appendix B.

ABSOLUTE AND NORMALIZED AMPLITUDES

We speak in the case of amplitudes A and P as defined in Eqs. (6) and (10) of *absolute amplitudes*. It is common practice to renormalize amplitudes and to express them in percentage according to Eq. (14):

$$\mathcal{A}_{n\mu}^{\%} = \frac{\mathcal{A}_{n\mu}}{\sum_m \mathcal{A}_{m\mu}} 100, \quad (14)$$

as a convenient way to compare them. This advantage has to be balanced against the fact that because of Eq. (14) amplitudes are no longer independent of the parameter set chosen.

Only if orthogonal vectors \mathbf{v}_n are used, the sum $\sum_n P_{nn}^\mu$ [compare with Eq. (9)] will become equal to one as can be seen when inserting Eqs. (11) and (10) into Eq. (9). In this case, the element P_{nn}^μ represents the fractional contribution of the internal mode \mathbf{v}_n to the normal mode vibration $\mathbf{1}_\mu$, which is schematically indicated in Figure 3(a). Usually, internal modes \mathbf{v}_n are not orthogonal and,

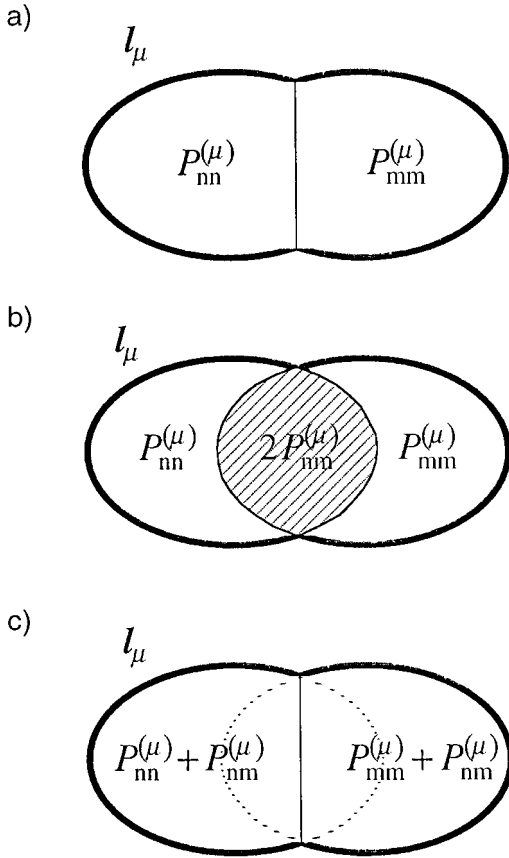


FIGURE 3. Symbolic characterization of a normal mode I_μ of a two-dimensional vibrational problem in terms of two internal vibrations \mathbf{v}_n and \mathbf{v}_m . (a) For orthogonal vectors \mathbf{v}_n and \mathbf{v}_m ($P_{nm}^\mu = 0$), amplitudes P_{nn}^μ and P_{mm}^μ add up to one. (b) If \mathbf{v}_n and \mathbf{v}_m are not orthogonal, P_{nm}^μ (shaded overlap region) is not equal to zero and P -type amplitudes do not add up to one. (c) Defining new P -type amplitudes $\tilde{P}_{nn}^\mu = P_{nn}^\mu + \tilde{P}_{nm}^\mu$ and $\tilde{P}_{mm}^\mu = P_{mm}^\mu + P_{nm}^\mu$, overlap vanishes and amplitudes again add to one.

then, the representation of Figure 3(b) applies, i.e., the density matrix element P_{nm}^μ is used for defining the contributions of both \mathbf{v}_n and \mathbf{v}_m to the normal mode I_μ . To retrieve the meaning of P_{nn}^μ in Figure 3(a), one can sum the off-diagonal elements P_{nm}^μ into the diagonal elements P_{nn}^μ and define in this way a new density matrix $\tilde{P}_{nn}^\mu = \sum_m P_{nm}^\mu$ [6] and, then, it can easily be shown that $\sum_n \tilde{P}_{nn}^\mu = 1$ for any set of nonorthogonal internal mode vectors \mathbf{v}_n [compare with Fig. 3(c)]. It can happen that some of the new matrix elements \tilde{P}_{nn}^μ are no longer positive [6], which makes their interpretation difficult. Therefore, we refrain from using matrix \tilde{P} .

NOTATION FOR DIFFERENT TYPES OF AMPLITUDES

Figure 4 summarizes the possible definitions of amplitudes $A_{n\mu}$ or density matrix elements P_{nn}^μ . Considering that one can choose between two different internal mode vectors \mathbf{v}_n (Av and Cv on the x -axis of Fig. 4), according to Eqs. (6) and (10) between two weighting coefficients A and P (y -axis of Fig. 4) and according to Eq. (13) between three different metrics \mathbf{O} (S, M, F on the z -axis of Fig. 4), there are 12 possibilities, which have to be tested:

$$\mathbf{O} = \mathbf{S} \quad \begin{cases} \text{AvAS} & \text{AvPS} \\ \text{CvAS} & \text{CvPS} \end{cases} \quad (15)$$

$$\mathbf{O} = \mathbf{M} \quad \begin{cases} \text{AvAM} & \text{AvPM} \\ \text{CvAM} & \text{CvPM} \end{cases} \quad (16)$$

$$\mathbf{O} = \mathbf{f} \quad \begin{cases} \text{AvAF} & \text{AvPF} \\ \text{CvAF} & \text{CvPF} \end{cases} \quad (17)$$

If amplitudes expressed in % are used, this will be indicated by the superscript “%.”

Characteristic Fragment Frequencies

The determination of characteristic fragment frequencies ω_n associated with the structural unit ϕ_n is a major, yet not satisfactorily solved task of vibrational spectroscopy. This has to do with the fact that the motion of a molecular fragment ϕ_n is

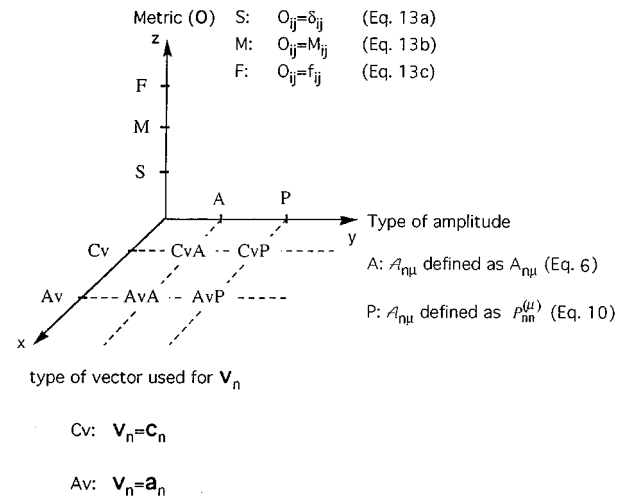


FIGURE 4. The 12 possible definitions of amplitudes determined by the choice of (a) internal vibration vectors \mathbf{v}_n (Cv or Av on x -axis), (b) the type of amplitude (A or P on y -axis), and (c) the metric \mathbf{O} (S, M, f on z -axis).

always coupled to the motions of the other structural units or fragments of the molecule. The measured frequencies are the ones arising from coupled motions of several or all fragments of the molecule. However, in some cases, the couplings between the different fragment motions are not so large so that it is possible to characterize a vibrational motion and its corresponding frequency as predominantly originating from the internal vibration of one particular fragment. Due to the nature of electronic structure and the conservation of the properties of certain structural elements in different molecules, similar characteristic fragment frequencies can be observed for the same structural unit in different molecules. Today, it is considered as an experimental fact that there are stable characteristic frequencies of molecular fragments that do not change from one molecule to the other [1]. In the literature, there are numerous attempts to generalize the concept of a characteristic fragment frequency ω_n , of which we will discuss just three different alternatives [2, 3, 11, 13].

1. A serious attempt of associating normal mode frequency ν_{μ}^{exp} with characteristic fragment frequency ν_n^{exp} was published by McKean who investigated the stretching mode of the CH group in various hydrocarbons [13]. This author solved the problem of mode-mode coupling between internal modes by *D*-substitution of all H atoms but the one considered thus increasing mass differences and reducing the amount of intramolecular mode-mode coupling. His approach led to characteristic CH stretching frequencies in different molecules and, by this, to an unique insight into the nature of the CH bond under different situations (compare with the outer cycle of Fig. 1). Certainly, it is possible to obtain other characteristic fragment frequencies in a systematic way although an enormous amount of synthetic work is involved to get suitable isotopomers in each case. In addition, the measured fragment frequencies will always be contaminated by some residual coupling. Therefore, one can predict that it is hardly possible to solve, just by experimental means, the problem of determining fragment-specific frequencies.

2. Theory provides a better basis to determine characteristic fragment frequencies ω_n . For

example, one could consider to calculate ω_n as an appropriate average of the normal mode frequencies ω_{μ} according to [3]:

$$\omega_n^2 = \sum_{\mu} \mathcal{A}_{n\mu} \omega_{\mu}^2 \quad (18)$$

using suitable amplitudes $\mathcal{A}_{n\mu}$. However, the deficiency of Eq. (18) is that there is no direct connection (e.g., in form of a dynamic principle) between the internal mode vector \mathbf{v}_n and the characteristic fragment frequency ω_n . The intrinsic frequencies suggested by Boatz and Gordon [11] belong to the class of internal frequencies defined by Eq. (18) and we have already shown in article II [3] that they, although useful for many acyclic molecules, are problematic in general.

3. Suppose that a normal mode \mathbf{l}_{μ} is dominated by an internal mode \mathbf{v}_n associated with the fragment ϕ_n . There are two factors that can influence the deviation $\delta\omega_{\mu}$ of the normal mode frequency ω_{μ} from the fragment mode frequency ω_n as indicated by the symbolic formula (19):

$$\delta\omega_{\mu} = \delta\omega_{\mu}(\text{mass}) + \delta\omega_{\mu}(\text{force}), \quad (19)$$

\downarrow
 large

\downarrow
 large

\downarrow
 small

where in the normal case the deviation is dominated by the mass effect rather than changes in the electronic structure. A prerequisite for obtaining *stable* internal modes ω_n is the proper separation of mass and electronic effect. As shown in article I [2], this requirement is fulfilled for the adiabatic mode vectors $\mathbf{v}_n = \mathbf{a}_n$, which represent the internal vibration of molecular fragments ϕ_n . Since the adiabatic mode vectors are based on a clear dynamical principle, their use should clarify which of the possible definitions of $\mathcal{A}_{n\mu}$ leads to the better correlation with $\Delta\omega_{n\mu}$ according to the criteria discussed in the second section.

Analysis and Comparison of Amplitudes $\mathcal{A}_{n\mu}$

Generally, there are two major uses of amplitudes $\mathcal{A}_{n\mu}$. First, they are needed to compare normal mode frequencies ω_{μ} with internal mode frequencies ω_n and to extract in this way chemically

useful information out of measured or calculated vibrational spectra. This is of major concern in this work and, therefore, we will concentrate on this objective. Second, one can characterize calculated normal modes \mathbf{l}_μ in terms of internal modes \mathbf{v}_n using amplitudes $\mathcal{A}_{n\mu}$. So far, this was done in the PED analysis [4–7], however, it is worthwhile to investigate whether some of the shortcomings of the PED analysis can be compensated by replacing P matrix elements by amplitudes \mathcal{A} . In addition, one could think of using amplitudes \mathcal{A} to determine internal mode frequencies ω_n according to Eq. (18). As mentioned, this approach is problematic and, therefore, we will refer to (18) only in so far as we compare intrinsic frequencies defined in this way with other internal frequencies. Hence, the major objective of this section will be the comparison of normal mode frequencies with internal mode frequencies using one of the definitions of an amplitude given in the third section.

On pure theoretical grounds, we can approach the question of which of the 12 amplitudes given in Eqs. (15)–(17) is the most suitable one for the task of comparing ω_μ with ω_n or decomposing \mathbf{l}_μ in terms of \mathbf{v}_n , in a stepwise manner following the three axes x , y , and z in Figure 4.

COMPARISON OF a-VECTORS WITH c-VECTORS

This has been explicitly done in article II [3], where it was shown that c-vectors suffer from the constrain $\mathbf{BC} = \mathbf{I}$. Amplitudes $A_{n\mu}$ calculated with c-vectors should be unstable with regard to changes in the parameters describing a molecule and, therefore, they should not be suited for a comparison of normal modes and internal modes. This excludes the six $C_v \dots$ amplitudes of the pool of amplitudes suggested in Eqs. (15)–(17).

COMPARISON OF A-TYPE AND P-TYPE AMPLITUDES

In the third section, it was stated that A -type amplitudes should be more useful than P -type amplitudes since, contrary to the latter, they are not parameter set dependent. Apart from this, it is not clear how to use matrix P for the comparison of normal and internal modes since this could be done by (a) considering just the diagonal elements of \mathbf{P} , (b) summing off-diagonal elements into the diagonal [6], or (c) using some other way of considering all rather than just diagonal elements. It is

known that (b) leads sometimes to negative diagonal elements, which is difficult to interpret [6]. Mostly, approach (a) is used even though it does not contain the full information covered by the \mathbf{P} matrix. On theoretical grounds, \mathbf{A} -type amplitudes are clearly superior to \mathbf{P} -type amplitudes, which excludes the six \mathbf{P} -based amplitude definitions of Eqs. (15)–(17).

COMPARISON OF DIFFERENT METRICS \mathbf{O}

A spatial comparison of two vectors or functions, although common practice when one considers dipole moments, orbitals, etc., provides little information in the case of the dynamic process of vibrating molecules. Therefore, it is more useful to use as metric matrix either the mass matrix \mathbf{M} (kinematic comparison) or the force constant matrix \mathbf{f} (dynamic comparison).

In summary, of the 12 possible amplitudes given in Eqs. (15)–(17), only two, namely, AvAM and AvAF, which compare normal modes and internal modes using adiabatic vectors \mathbf{a}_n in connection with the amplitude definition of Eq. (6) and the metric \mathbf{M} and \mathbf{f} , seem to be suitable on theoretical grounds for a comparison. In Appendix B, it is shown that both AvAM and AvAF can be obtained from equations of motion [see Eq. (B12); for $\mathbf{v}_n = \mathbf{a}_n$, $A_{n\mu}^{(\mathbf{M})} = \text{AvAM}$ and $A_{n\nu}^{(\mathbf{f})} = \text{AvAF}$].

Conclusions

The characterization of normal modes (CNM) is a major goal in vibrational spectroscopy to extract chemical useful information on structure and bonding in molecules out of measured (or calculated) vibrational spectra and, therefore, its realization has been discussed in this work. The elements of the CNM analysis are normal modes, elementary internal modes associated with a molecular fragment or structural subunit ϕ_n described by internal parameters ζ_n , and amplitudes $\mathcal{A}_{n\mu}$, which provide the basis for a direct comparison of normal modes and internal modes.

A general definition of amplitude $\mathcal{A}_{n\mu}$ in the form of [Eq. (6)] has been given and compared with the \mathbf{P} matrix elements of the PED analysis [4–7]. Taking both A -type and P -type amplitudes together and considering the different possibilities of chosen internal mode vectors (\mathbf{a}_n or \mathbf{c}_n) and metrics \mathbf{O} (\mathbf{S} , \mathbf{M} , \mathbf{f}), 12 different definitions for an

amplitude have been obtained [Eqs. (15)–(17)]. The theoretical analysis suggests that the use of Eq. (6) in connection with adiabatic internal motions and metric matrices \mathbf{M} and \mathbf{f} yielding amplitudes AvAM and AvAF should provide the best tools for comparing normal modes and internal modes within the CNM analysis.

In addition, procedures have been developed to test suitable amplitudes in ab initio calculations. Three possibilities have been discussed:

- 1. Amplitude vs. $\Delta\omega$ correlation:** Given all normal vibrational modes and internal vibrational modes of a molecule as well as their corresponding frequencies, the distribution of all amplitudes $\mathcal{A}_{n\mu}$ in dependence of differences $\Delta\omega_{n\mu} = \omega_n - \omega_\mu$ should be enveloped by a Lorentzian curve as shown in Figure 2. The scattering of $\mathcal{A}_{n\mu}$ in dependence of differences $\Delta\omega_{n\mu}$ outside or inside this enveloping curve provides a direct qualitative impression on the usefulness of the chosen amplitude and its underlying dynamical origin.
- 2. Uncertainty test of internal mode frequency:** While (1) provides a crude qualitative test, its quantification is obvious. The $\mathcal{A}_{n\mu} - \Delta\omega_{n\mu}$ correlation diagram indicates that deficiencies of the amplitude definition become apparent for points with large $\Delta\omega$ and large \mathcal{A} value. Accordingly, the quantity $h_{n\mu}$.

$$h_{n\mu} = \mathcal{A}_{n\mu} \Delta\omega_{n\mu}, \quad (20)$$

which has the dimension of a frequency and can be considered as an uncertainty of the internal mode frequency, provides a quantitative measurement of the usefulness of amplitude $\mathcal{A}_{n\mu}$. In the normal case, the uncertainty $h_{n\mu}$ should have small vanishing values while an accumulation of large $h_{n\mu}$ values indicates deficiencies of amplitudes $\mathcal{A}_{n\mu}$.

- 3. Stability test of \mathcal{A} with regard to variations in the parameter set used:** Amplitudes $\mathcal{A}_{n\mu}$ of the same internal motions associated with the same internal parameters ζ_n are calculated for a sequence of different parameter sets PSA, PSB, etc. The difference in amplitudes $\Delta\mathcal{A}_{n\mu} = |\mathcal{A}_{n\mu}(\text{PSA}) - \mathcal{A}_{n\mu}(\text{PSB})|$ is calculated for those internal motions covered by all parameter sets and summed over all nor-

mal modes \mathbf{l}_μ to obtain $\Delta\mathcal{A}$ as a bar spectrum for the internal parameters ζ_n considered. The spectrum $\Delta\mathcal{A} - \zeta_n$ provides a direct insight into the usefulness of the internal mode vectors \mathbf{v}_n and amplitudes $\mathcal{A}_{n\mu}$ within the CNM analysis.

These three tests seem to be appropriate for practical investigations and we will use them in article IV of this series [12].

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.

Appendix A. The Relationship Between $\mathcal{A}_{n\mu}$ and $\Delta\omega_{n\mu}$

The relationship between amplitude $\mathcal{A}_{n\mu}$ and $\Delta\omega_{n\mu}$ (difference between normal mode frequency ω_μ and characteristic fragment frequency ω_n) can be expressed by Eq. (A1):

$$\mathcal{A}_{n\mu} = \frac{1}{1 + \left(\frac{\omega_\mu^2 - \Omega_n^2}{\Gamma_n^2} \right)^2}, \quad (\text{A1})$$

where Ω_n is defined by

$$\Omega_n^2 \approx \frac{\langle \mathbf{v}_n | \mathbf{f} | \mathbf{v}_n \rangle}{\langle \mathbf{v}_n | \mathbf{M} | \mathbf{v}_n \rangle} \quad (\text{A2})$$

and represents an internal reference frequency, while Γ_n describes the coupling of the internal vibration \mathbf{v}_n under consideration with all other vibrations \mathbf{v}_m for $m \neq n$.

Equation (A1) can be derived by assuming a two-dimensional configuration space spanned by two elementary mode vectors \mathbf{v}_1 and \mathbf{v}_2 that for reasons of simplicity are considered to be orthogonal. Mode vector \mathbf{v}_1 describes the vibration of the molecular fragment ϕ_1 , which is described by the internal parameter ζ_1 , i.e., ζ_1 is the "leading parameter" of \mathbf{v}_1 [2]. Since a molecule with just two

vibrational degrees of freedom is not possible, one can consider all other vibrational degrees of freedom covered by \mathbf{v}_2 .

For a comparison of \mathbf{v}_1 with \mathbf{l}_μ ($\mu = 1, 2$), the amplitude $\mathcal{A}_{1\mu}$ has to be determined. The vibrational problem expressed by Eq. (A3)

$$\mathbf{fl} = \mathbf{Ml}\omega^2 \quad (\text{A3})$$

can be solved in the basis $\mathbf{v}_1, \mathbf{v}_2$ according to Eq. (A4):

$$\begin{pmatrix} f_{11} & f_{12} \\ f_{21} & f_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \omega^2, \quad (\text{A4})$$

where

$$f_{ij} = \langle \mathbf{v}_i | \mathbf{f} | \mathbf{v}_j \rangle \quad (\text{A5})$$

$$M_{ij} = \langle \mathbf{v}_i | \mathbf{M} | \mathbf{v}_j \rangle \quad i, j = 1, 2 \quad (\text{A6})$$

$$\mathbf{l}_\mu = c_{1\mu} \mathbf{v}_1 + c_{2\mu} \mathbf{v}_2. \quad (\text{A7})$$

Equation (A4) can be transformed into eigenvalue Eq. (A8):

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c'_1 \\ c'_2 \end{pmatrix} = \begin{pmatrix} c'_1 \\ c'_2 \end{pmatrix} \omega^2 \quad (\text{A8a})$$

$$\mathbf{Hc} = \omega^2 \mathbf{c}, \quad (\text{A8b})$$

with

$$\mathbf{H} = \mathbf{M}^{-1/2} \mathbf{f} \mathbf{M}^{-1/2} \quad (\text{A9})$$

$$\mathbf{c}' = \mathbf{M}^{1/2} \mathbf{c}. \quad (\text{A10})$$

If force and mass coupling between vectors \mathbf{v}_1 and \mathbf{v}_2 is vanishing small (i.e., \mathbf{M} and \mathbf{f} are almost diagonal), then one will observe a pure normal mode frequency ω_1 close to the unperturbed frequency Ω_1 associated with reference mode \mathbf{v}_1 :

$$\Omega_1^2 = H_{11} \approx \frac{\langle \mathbf{v}_1 | \mathbf{f} | \mathbf{v}_1 \rangle}{\langle \mathbf{v}_1 | \mathbf{M} | \mathbf{v}_1 \rangle}, \quad (\text{A11})$$

where the term pure is used in the sense that

$$\mathbf{l}_\mu = \mathbf{v}_1 \quad (\text{A12})$$

To solve Eq. (A8), the following relations have to be satisfied:

$$(\omega^2 - \Omega_1^2)(\omega^2 - H_{22}) = H_{12}^2 \quad (\text{A12a})$$

$$H_{12} c'_2 = (\omega^2 - \Omega_1^2) c'_1. \quad (\text{A12b})$$

According to Eq. (8), amplitude $\mathcal{A}_{\mu 1}$ for the comparison of reference mode \mathbf{v}_1 with normal mode \mathbf{l}_μ

is defined by Eq. (A13):

$$\mathcal{A} = \frac{\langle \mathbf{v}_1 | \mathbf{l} \rangle^2}{\langle \mathbf{v}_1 | \mathbf{v}_1 \rangle \langle \mathbf{l} | \mathbf{l} \rangle} = \frac{1}{1 + \left(\frac{c_2}{c_1} \right)^2}, \quad (\text{A13})$$

where the index μ has been dropped and Eq. (A7) has been used. Inserting Eqs. (A12a) and (A12b) into (A13) and assuming that

$$c'_2/c'_1 \approx c_2/c_1, \quad (\text{A14})$$

one obtains Eq. (A15):

$$\mathcal{A} = \frac{1}{1 + \left(\frac{\omega^2 - \Omega_1^2}{\Gamma^2} \right)}, \quad (\text{A15})$$

which can be generalized to yield Eq. (A1). In (A15), Γ represents a natural broadening frequency given by

$$\Gamma = H_{12}, \quad (\text{A16})$$

which in the case of Eq. (A1) is replaced by the average mixing term Γ_n . Equation (A1) leads to a Lorentzian (bell-shaped) curve [8].

Appendix B. Physical Meaning of Amplitudes $A_{n\mu}^{(S)}$, $A_{n\mu}^{(M)}$, and $A_{n\mu}^{(F)}$

Taking the definition of a general amplitude given in Eq. (8),

$$A_{n\mu}^{(R)} = \frac{(\mathbf{l}_{\mu'} \cdot \mathbf{v}_n)^2}{(\mathbf{l}_{\mu'} \cdot \mathbf{l}_{\mu})(\mathbf{v}_n \cdot \mathbf{v}_n)}, \quad (\text{B1})$$

where the superscript R indicates that the scalar product can be defined in different ways:

$$(\mathbf{a}, \mathbf{b}) = \begin{cases} \langle \mathbf{a} | \mathbf{I} | \mathbf{b} \rangle \\ \langle \mathbf{a} | \mathbf{f} | \mathbf{b} \rangle \\ \langle \mathbf{a} | \mathbf{M} | \mathbf{b} \rangle \end{cases} \quad (\text{B2})$$

(\mathbf{I} : unit matrix; spatial comparison; \mathbf{f} : force constant matrix in Cartesian coordinates; dynamic comparison; \mathbf{M} : mass matrix; kinetic comparison), one obtains three different types of amplitudes, namely, $A_{n\mu}^{(S)}$, $A_{n\mu}^{(M)}$, and $A_{n\mu}^{(F)}$, which can take any value between 0 and 1. The spatial overlap amplitudes $A_{n\mu}^{(S)}$ give information on the geometrical

relationship between vectors \mathbf{v}_n and \mathbf{I}_μ , while the physical meaning of amplitudes $A_{n\mu}^{(F)}$ and $A_{n\mu}^{(M)}$ is illustrated in this appendix.

Once the vibrational problem has been solved, one can express the total vibrational energy in terms of normal mode coordinates $Q_\mu(t)$:

$$E = \frac{1}{2} \sum_{\mu} \left(m_{\mu} \dot{Q}_{\mu}(t)^2 + k_{\mu} Q_{\mu}(t)^2 \right). \quad (\text{B3})$$

Inserting the general solution for the time dependence of normal coordinates $Q_\mu(t)$,

$$Q_{\mu}(t) = \frac{\dot{Q}_{\mu}(0)}{\omega_{\mu}} \sin \omega_{\mu} t + Q_{\mu}(0) \cos \omega_{\mu} t \quad (\text{B4})$$

into the energy expression (B3) leads to Eq. (B5):

$$E = \frac{1}{2} \sum_{\mu} \left(m_{\mu} \dot{Q}_{\mu}(0)^2 + k_{\mu} Q_{\mu}(0)^2 \right). \quad (\text{B5})$$

At $t = 0$, an internal vibration described by vector \mathbf{v}_n is triggered in the molecular fragment ϕ_n by a slight distortion of the associated internal parameter ζ_n in the sense of the leading parameter principle (see article I [2]). The initial conditions for the displacement vector \mathbf{x} at $t = 0$ can be given by [compare with Eq. (4) of article I [2]]

$$\mathbf{x}(0) = \mathbf{v}_n \dot{q}_n^*(0) \quad (\text{B6a})$$

$$\dot{\mathbf{x}}(0) = \mathbf{v}_n \ddot{q}_n^*(0). \quad (\text{B6b})$$

When the molecule is distorted according to (B6a) and (B6b), it is possible to calculate which normal modes are activated by this displacement.

The initial conditions expressed in normal coordinates are given by Eqs. (B7):

$$\mathbf{x}(0) = \sum_v \mathbf{I}_v Q_v(0) = \mathbf{v}_n q_n^*(0) \quad (\text{B7a})$$

$$\dot{\mathbf{x}}(0) = \sum_v \mathbf{I}_v \dot{Q}_v(0) = \mathbf{v}_n \dot{q}_n^*(0). \quad (\text{B7b})$$

Multiplying (B7a) and (B7b) from the left by $\langle \mathbf{I}_\mu | \mathbf{f} | \mathbf{v}_n \rangle$ and $\langle \mathbf{I}_\mu | \mathbf{M} | \mathbf{I}_\mu \rangle$, $Q_\mu(0)$ and $\dot{Q}_\mu(0)$ can be expressed as functions of $q_n^*(0)$ and $\dot{q}_n^*(0)$:

$$Q_{\mu}(0) = \frac{\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{v}_n \rangle}{\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{I}_{\mu} \rangle} q_n^*(0) \quad (\text{B8a})$$

$$\dot{Q}_{\mu}(0) = \frac{\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{v}_n \rangle}{\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{I}_{\mu} \rangle} \dot{q}_n^*(0). \quad (\text{B8b})$$

By inserting (B8a) and (B8b) into (B5), one obtains Eq. (B9):

$$E = \frac{1}{2} \sum_{\mu} \left(m_{\mu} \frac{\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{v}_n \rangle^2}{\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{I}_{\mu} \rangle^2} \dot{q}_n^*(0)^2 + k_{\mu} \frac{\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{v}_n \rangle^2}{\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{I}_{\mu} \rangle^2} q_n^*(0)^2 \right), \quad (\text{B9})$$

where m_{μ} is recognized as $\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{I}_{\mu} \rangle$, and k_{μ} , as $\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{I}_{\mu} \rangle$. Equation (B9) can be rearranged to

$$E = \frac{1}{2} \sum_{\mu} \frac{\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{v}_n \rangle^2}{\langle \mathbf{I}_{\mu} | \mathbf{M} | \mathbf{I}_{\mu} \rangle \langle \mathbf{v}_n | \mathbf{M} | \mathbf{v}_n \rangle} \langle \mathbf{v}_n | \mathbf{M} | \mathbf{v}_n \rangle \dot{q}_n^*(0)^2 + \frac{1}{2} \sum_{\mu} \frac{\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{v}_n \rangle^2}{\langle \mathbf{I}_{\mu} | \mathbf{f} | \mathbf{I}_{\mu} \rangle \langle \mathbf{v}_n | \mathbf{f} | \mathbf{v}_n \rangle} \langle \mathbf{v}_n | \mathbf{f} | \mathbf{v}_n \rangle q_n^*(0)^2. \quad (\text{B10})$$

With the help of the definition of $A_{n\mu}^{(R)}$ given in Eq. (B1), one finally obtains

$$E = \frac{1}{2} \sum_{\mu} \left(A_{n\mu}^{(M)} M_n \dot{q}_n^*(0)^2 + A_{n\mu}^{(F)} k_n q_n^*(0)^2 \right), \quad (\text{B11})$$

where $\langle \mathbf{v}_n | \mathbf{M} | \mathbf{v}_n \rangle = M_n$ is the effective mass and $\langle \mathbf{v}_n | \mathbf{f} | \mathbf{v}_n \rangle = k_n$ the effective force constant of the internal vibration represented by vector \mathbf{v}_n .

Equation (B11) can be simplified to

$$E = \sum_{\mu} \left(A_{n\mu}^{(M)} T_n + A_{n\mu}^{(F)} V_n \right), \quad (\text{B12})$$

where T_n and V_n are the kinetic and potential energies stored in the internal motion associated with vector \mathbf{v}_n . Equation (B12) presents the basis for a discussion of the physical meaning of amplitudes $A_{n\mu}^{(M)}$ and $A_{n\mu}^{(F)}$: It reveals how kinetic energy T_n and potential energy V_n initially stored in the internal vibration \mathbf{v}_n are redistributed over the normal modes \mathbf{I}_μ . In principle, a normal mode \mathbf{I}_μ can assess energy by extracting it either from the kinetic energy or the potential energy of the internal vibration \mathbf{v}_n . The ability of the normal mode \mathbf{I}_μ to use one of these ways is determined by the amplitudes $A_{n\mu}^{(M)}$ and $A_{n\mu}^{(F)}$. Accordingly, Eq. (B12) can explain the dynamic origin of a normal mode \mathbf{I}_μ . For example, if one assumes that $A_{n\mu}^{(F)} = 0$, $A_{n\mu}^{(M)} = 1$ for normal mode \mathbf{I}_μ and $A_{n\nu}^{(F)} = A_{n\nu}^{(M)} = 0$ for all other normal mode \mathbf{I}_ν , then the vibrational energy of internal mode \mathbf{v}_n will be totally transferred to \mathbf{I}_μ , thus activating its vibrations. The nature of the vibrational mode \mathbf{I}_μ will be totally determined by the distribution of masses in the

molecule and, therefore, one can say that the vibrational mode I_μ kinetically originates from the internal vibration \mathbf{v}_n .

The nature of the vibrational mode I_μ will be totally determined by the electronic structure of the molecule if $A_{n\mu}^{(F)} = 1$, $A_{n\mu}^{(M)} = 0$, and $A_{n\nu}^{(F)} = A_{n\nu}^{(M)} = 0$. In this case, one can say that normal mode I_μ electronically originates from the internal vibration \mathbf{v}_n .

References

1. (a) G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945). (b) K. Nakamishi and P. H. Soloman, *Infrared Absorption Spectroscopy* (Holden-Day, San Francisco, 1977). (c) N. B. Colthup, L. N. Daly, and S. E. Wilberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, 1990).
2. Z. Konkoli and D. Cremer, *Int. J. Quantum. Chem.* **67**, 1 (1998).
3. Z. Konkoli, A. Larsson, and D. Cremer, *Int. J. Quantum. Chem.* **67**, 11 (1998).
4. P. Torkington, *J. Chem. Phys.* **17**, 457 (1949).
5. Y. Morino and K. Kuchitsu, *J. Chem. Phys.* **20**, 1809 (1952).
6. P. Pulay and F. Török, *Acta Chim. Hung.* **47**, 273 (1966).
7. G. Keresztury and G. Jalsovszky, *J. Mol. Struct.* **10**, 304 (1971).
8. J. M. Hollas, *High Resolution Spectroscopy* (Butterworths, London, 1982).
9. R. J. Malhiot and S. M. Ferigle, *J. Chem. Phys.* **22**, 717 (1954).
10. (a) N. Neto, *Chem. Phys.* **91**, 89, 101 (1984). (b) N. Neto, *Chem. Phys.* **87**, 43 (1984).
11. J. A. Boatz and M. S. Gordon, *J. Phys. Chem.* **93**, 1819 (1989).
12. Z. Konkoli, A. Larsson, and D. Cremer, *Int. J. Quantum. Chem.* **67**, 41 (1998).
13. D. C. McKean, *Chem. Soc. Rev.* **7**, 399 (1978).