

# Decomposition of Normal-Coordinate Vibrational Frequencies

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A decomposition scheme for the partitioning of normal-coordinate vibrational frequencies into individual internal-coordinate "intrinsic" frequencies is presented. This scheme assigns to each internal coordinate a frequency that is representative of a vibration described solely by motion of that particular coordinate. This facilitates the interpretation of harmonic vibrational frequencies and their associated normal-coordinate displacements, especially in those cases where the normal coordinates are best described by the coupling of several internal coordinates. The utility of the method is demonstrated via application to several simple hydrides and cycloalkanes, using ab initio SCF molecular structures and Cartesian force constant matrices.

## I. Introduction

The concept of the chemical bond is central to all of chemistry.<sup>1</sup> Therefore, the characterization of a bond is of fundamental importance to the understanding of chemical problems. Among the most familiar quantities associated with a bond are its strength (i.e., energy), length, and vibrational force constant. The latter quantity has proven to be of utmost utility in the identification of specific bonds within a given molecule via infrared spectroscopy.<sup>2</sup> The computation of theoretical vibrational frequencies<sup>3</sup> and infrared intensities<sup>4</sup> has also been instrumental in the elucidation of bond types within molecules. Therefore, the characterization of chemical bonds in terms of parameters such as force constants and vibrational frequencies is of great importance.

Perhaps the most popular method of describing molecular vibrations is within the setting of the harmonic force field approximation. In this scheme, the potential energy surface of nuclear motion (in the vicinity of a stationary point) is assumed to be adequately described by a quadratic Taylor series expansion. Diagonalization of the mass-weighted matrix of Cartesian second derivatives of the energy leads to the determination of harmonic frequencies and normal coordinates.<sup>5</sup> While the description of molecular vibrations in terms of normal coordinates is well understood,<sup>5a</sup> the normal-coordinate analysis scheme does not easily lend itself to the assignment of frequencies to individual internal coordinates, since the vibrational motions described by normal coordinates are symmetry-adapted; i.e., each normal-coordinate motion transforms as one of the irreducible representations of the molecular point group. Consequently, in general a particular internal coordinate will contribute to the description of several normal modes, and each normal mode is delocalized in much the same way that canonical molecular orbitals are delocalized.

This work is directed toward the development of a general scheme for assigning vibrational "frequencies" to individual internal coordinates. The analysis presented here is in many ways analogous to the calculation of localized orbitals<sup>6</sup> from the canonical SCF orbitals determined in a Hartree-Fock computation. In both cases, an entity (a molecular orbital or normal mode

vibration) that is delocalized over the entire molecule is transformed into a localized counterpart. Thus, in the case of localized molecular orbital transformations, the symmetry-adapted canonical SCF MO's become bonds and lone pairs, which are more amenable to chemical interpretation and intuition. Likewise, in the vibrational decomposition scheme presented in this paper, the frequencies corresponding to symmetry-adapted normal coordinates are transformed into "intrinsic" frequencies, which represent the sum of the contributions of all normal modes of vibration to a particular internal coordinate. This process thus yields a single vibrational frequency for each internal coordinate.

Section II summarizes the computational procedure used in this study. The computed intrinsic frequencies are presented and discussed in section III. The major conclusions of this work are given in section IV.

## II. Computational Approach

All molecular structures and harmonic force fields were computed at the Hartree-Fock SCF level, using the analytical gradient techniques in GAUSSIAN82<sup>7</sup> and the 3-21G<sup>8</sup> basis set. The decomposition scheme applied to the normal coordinates and their corresponding vibrational frequencies is outlined below and has been incorporated into the GAMESS<sup>9</sup> program. In the following, **M** and  **$\tilde{V}$**  will denote matrices and vectors, respectively. **M**<sup>t</sup> and **M**<sup>-1</sup> will indicate the transpose and inverse, respectively, of a matrix **M**. For ease of discussion, a nonlinear molecule (and hence  $3N - 6$  vibrational degrees of freedom) will be assumed. The generalization to the case of a linear molecule with  $3N - 5$  vibrations will be obvious. (Some of the following derivation follows that presented by several authors<sup>5,10</sup> and is summarized here for ease of reference.)

For a molecule consisting of  $N$  atoms, the vector of  $3N$  Cartesian coordinates is defined as

$$\vec{X}^t = (x_1, y_1, z_1, \dots, x_N, y_N, z_N) \quad (1)$$

(In general, the  $i$ th element of  $\vec{X}$  will simply be referred to as  $x_i$ .)

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(10) See, for example: (a) Woodward, L. A. *Introduction to the Theory of Molecular Vibrations and Vibrational Spectroscopy*; Oxford University Press: London, 1972. (b) Pulay, P. Direct Use of the Gradient for Investigating Molecular Energy Surfaces. In *Applications of Electronic Structure Theory*; Schaefer, H. F. III, Ed.; Plenum Press: New York, 1977. (c) Fogarasi, G.; Pulay, P. Ab Initio Calculation of Force Fields and Vibrational Spectra. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier Science Publishing Co., Inc.: New York, 1985; Vol. 14.

The vector of internal coordinates  $\bar{R}$  is similarly defined as

$$\bar{R}^t = (r_1, r_2, \dots, r_s) \quad (2)$$

where  $S = 3N - 6$ . The matrix  $\mathbf{B}$  transforms the Cartesian coordinates  $\bar{X}$  into the internal coordinates  $\bar{R}$

$$\bar{R} = \mathbf{B}\bar{X} \quad (3)$$

and is of dimension  $S \times 3N$ . The Cartesian force constant matrix  $\mathbf{f}$  is defined as

$$f_{ij} = \partial^2 E / \partial x_i \partial x_j \quad (4a)$$

where  $E$  is the internal energy of the system. Likewise, the internal-coordinate force constant matrix  $\mathbf{F}$  is defined as

$$F_{ij} = \partial^2 E / \partial r_i \partial r_j \quad (4b)$$

and is related to  $\mathbf{f}$  through the following transformations:

$$\mathbf{F} = (\bar{\mathbf{B}}^{-1})^t \mathbf{f} \bar{\mathbf{B}}^{-1} \quad (5a)$$

$$\mathbf{f} = \bar{\mathbf{B}}^t \mathbf{F} \bar{\mathbf{B}} \quad (5b)$$

In eq 5a the matrix  $\bar{\mathbf{B}}$  is the augmented  $\mathbf{B}$  matrix. The additional six rows appended to  $\mathbf{B}$  to obtain  $\bar{\mathbf{B}}$  represent the Eckart conditions describing translational and rotational invariance.<sup>11</sup> Thus, the dimensions of  $\bar{\mathbf{B}}$  are  $(S + 6) \times 3N$ .

Harmonic frequencies and normal-coordinate displacements are determined via diagonalization of  $\mathbf{f}'$ , the mass-weighted<sup>5b</sup> Cartesian force constant matrix:

$$\mathbf{f}'\mathbf{L} = \mathbf{L}\mathbf{\Lambda} \quad (6)$$

where  $\mathbf{L}$  is the matrix of eigenvectors (i.e., the normal-coordinate displacement vectors) and  $\Lambda_{ij} = \delta_{ij}\lambda_i$  is the diagonal matrix of eigenvalues (i.e., the harmonic vibrational frequencies).  $\mathbf{f}'$  is defined as

$$\mathbf{f}' = (\mathbf{M}^{-1/2})^t \mathbf{f} \mathbf{M}^{-1/2} \quad (7)$$

where  $(\mathbf{M}^{-1/2})_{ij} = \delta_{ij}m_i^{-1/2}$  is the diagonal matrix of reciprocal square roots of the atomic masses  $m_i$ . Equation 6 can be expressed as

$$\mathbf{\Lambda} = \mathbf{L}'\mathbf{f}'\mathbf{L} \quad (8a)$$

or, in terms of the unweighted force constant matrix

$$\mathbf{\Lambda} = \mathbf{l}'\mathbf{f}\mathbf{l} \quad (8b)$$

where  $\mathbf{l} = \mathbf{M}^{-1/2}\mathbf{L}$ .

The transformations described by eq 5 can be done by using the unaugmented matrix  $\mathbf{B}$  rather than  $\bar{\mathbf{B}}$ . Substituting eq 5b (and using  $\mathbf{B}$  in place of  $\bar{\mathbf{B}}$ ) into eq 8b yields

$$\mathbf{\Lambda} = \mathbf{l}'(\mathbf{B}'\mathbf{F}\mathbf{B})\mathbf{l} \quad (9a)$$

$$= \mathbf{D}'\mathbf{F}\mathbf{D} \quad (9b)$$

where the matrix  $\mathbf{D}$ , given by

$$\mathbf{D} = \mathbf{B}\mathbf{l} \quad (10)$$

of dimension  $S \times 3N$  has been used.

Equation 9b in scalar form is

$$\lambda_i = \sum_m \sum_n D_{mi} F_{mn} D_{ni} \quad (11)$$

Using this equation, we define the *vibrational density matrices*  $\mathbf{P}^i$  as<sup>12</sup>

$$P_{mn}^i = D_{mi} F_{mn} D_{ni} / \lambda_i \quad (12)$$

TABLE I: Harmonic and Intrinsic Frequencies of Water<sup>a</sup>

| Harmonic Frequencies  |                         |   |      |      |
|---|-------------------------|---|------|------|
| freq  | normal mode description |   |      |      |
| 1799  | H-O-H bend              |   |      |      |
| 3813  | O-H stretch             |   |      |      |
| 3947  | O-H stretch             |   |      |      |
| Diagonal Elements of the Vibrational Density Matrices ( $\mathbf{P}^i$ ) <sup>b</sup> |                         |   |      |      |
| internal coord  | intrinsic freq          | diagonal elements at the following harmonic frequencies |      |      |
|   |                         | 1799  | 3813 | 3947 |
| H-O-H bend  | 1812                    | 1.03  | 0.00 | 0.00 |
| O-H stretch   | 3878                    | 0.02  | 0.50 | 0.49 |
|   |                         | 0.02  | 0.50 | 0.49 |

<sup>a</sup> In  $\text{cm}^{-1}$ . The elements of the  $\mathbf{P}^i$  matrices are unitless. <sup>b</sup> See text.

$P_{mn}^i$  is analogous to the overlap population matrix<sup>13</sup> encountered in ab initio SCF energy calculations and is related to the kinetic and potential energy distributions<sup>12</sup> introduced in earlier works. (Because the six  $\lambda_i$  corresponding to translations and rotations are zero, the corresponding  $\mathbf{P}^i$  matrices are not calculated.) The diagonal elements  $P_{mm}^i$  represent the contribution of internal coordinate  $r_m$  to the normal-coordinate force constant  $k_i$ . Note that

$$\lambda_i = \sum_m \sum_n P_{mn}^i \lambda_i \quad \text{i.e.,} \quad \sum_m \sum_n P_{mn}^i = 1 \quad (13)$$

Finally, we define the *intrinsic vibrational frequencies*  $\nu_n$  as

$$\nu_n = \sum_m \sum_i P_{mi}^n \lambda_i \quad (14a)$$

Each  $\nu_n$  represents the total contribution of an internal coordinate  $r_n$  to the normal-coordinate frequencies. Note that the quantity  $\nu_n^i$  given by

$$\nu_n^i = \sum_m P_{mi}^n \lambda_i \quad (14b)$$

represents the contribution of internal coordinate  $r_n$  to normal coordinate  $i$ .<sup>12a</sup>

The intrinsic frequencies can be calculated without computing the  $\mathbf{P}^i$ . This is done by combining eq 12 and 14a to give

$$\nu_n = \sum_m \sum_i D_{mi} F_{mn} D_{ni} \quad (14c)$$

The matrix  $\bar{\mathbf{B}}^{-1}$  in eq 5a is obtained as follows. Initially, the  $\mathbf{G}$  matrix is constructed:

$$\mathbf{G} = \bar{\mathbf{B}}\mathbf{m}^{-1}\bar{\mathbf{B}}^t \quad (15)$$

where  $\mathbf{m}^{-1}$  is the  $3N \times 3N$  matrix containing the reciprocals of the atomic masses along the diagonal and zeroes elsewhere.  $\mathbf{G}$  as constructed is then a  $(S + 6) \times (S + 6)$  real symmetric matrix and can be routinely diagonalized:

$$\mathbf{G}\mathbf{K} = \mathbf{K}\mathbf{e} \quad (16)$$

where  $\mathbf{K}$  and  $\mathbf{e}$  are the matrices of eigenvectors and eigenvalues, respectively.  $\mathbf{G}^{-1}$  may then be calculated from

$$\mathbf{G}^{-1} = \mathbf{K}\mathbf{e}^{-1}\mathbf{K}^t \quad (17a)$$

Rewritten in scalar form, this becomes

$$G_{ij}^{-1} = \sum_n K_{ni} K_{nj} / e_n \quad (17b)$$

since  $\mathbf{e}$  is diagonal.

Taking the inverse of both sides of eq 15 yields

$$\begin{aligned} \mathbf{G}^{-1} &= (\bar{\mathbf{B}}\mathbf{m}^{-1}\bar{\mathbf{B}}^t)^{-1} \\ &= (\bar{\mathbf{B}}^{-1})^t \mathbf{m} \bar{\mathbf{B}}^{-1} \end{aligned} \quad (18)$$

which can be rearranged to give the following expression for  $\bar{\mathbf{B}}^{-1}$ :

$$\bar{\mathbf{B}}^{-1} = \mathbf{m}^{-1}\bar{\mathbf{B}}^t\mathbf{G}^{-1} \quad (19)$$

(11) Eckart, C. *Phys. Rev.* **1935**, *47*, 552-558.  
(12) (a) The kinetic and potential energy distribution matrix  $\mathbf{M}$  (ref 12b) is calculated from  $\mathbf{P}^i$  via  $M_{im} = \sum_n P_{mn}^i$ . (b) Pulay, P.; Török, F. *Acta Chim. Acad. Sci. Hung.* **1966**, *47*, 273-279. (c) Morino, Y.; Kuchitsu, K. *J. Chem. Phys.* **1952**, *20*, 1809-1810. (d) Keresztury, G.; Jalsovszky, Gy. *J. Mol. Struct.* **1971**, *10*, 304-305.

(13) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833-1840. (b) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841-1846.

TABLE II: Harmonic and Intrinsic Frequencies of Ammonia<sup>a</sup>

| Harmonic Frequencies   |                |   |       |       |      |       |       |
|--|----------------|---|-------|-------|------|-------|-------|
| freq   |                | normal mode description                                 |       |       |      |       |       |
| 855  |                | H-N-H bend  |       |       |      |       |       |
| 1858 (2)   |                | H-N-H bend  |       |       |      |       |       |
| 3644   |                | N-H stretch   |       |       |      |       |       |
| 3800 (2)   |                | N-H stretch   |       |       |      |       |       |
| Diagonal Elements of the Vibrational Density Matrices ( $P^i$ ) <sup>b</sup> |                |   |       |       |      |       |       |
| internal coord   | intrinsic freq | diagonal elements at the following harmonic frequencies |       |       |      |       |       |
|  |                | 855   | 1858  | 1858  | 3644 | 3800  | 3800  |
| H-N-H bend   | 1595           | -0.29   | 0.72  | 0.00  | 0.01 | -0.03 | 0.00  |
| H-N-H bend   | 1595           | -0.29   | -0.36 | 0.63  | 0.01 | 0.02  | 0.03  |
| H-N-H bend   | 1595           | -0.29   | -0.36 | -0.63 | 0.01 | 0.02  | -0.03 |
| N-H stretch  | 3749           | 0.05  | -0.02 | -0.03 | 0.58 | 0.43  | -0.74 |
| N-H stretch  | 3749           | 0.05  | -0.02 | 0.03  | 0.58 | 0.43  | 0.73  |
| N-H stretch  | 3749           | 0.05  | 0.03  | 0.00  | 0.58 | -0.85 | 0.00  |

<sup>a</sup> In  $\text{cm}^{-1}$ . The elements of the  $P^i$  matrices are unitless. The degeneracies of the harmonic frequencies are indicated in parentheses. <sup>b</sup> See text.

We now illustrate the calculation of intrinsic frequencies  $\nu_n$  for several small hydrides.

**H<sub>2</sub>O, NH<sub>3</sub>.** Table I summarizes the intrinsic and normal-coordinate frequencies  $\nu_n$  for H<sub>2</sub>O. Since H<sub>2</sub>O is a nonlinear triatomic molecule, three internal coordinates (the two O-H stretches and the H-O-H bend) were used in the analysis. The O-H stretch and H-O-H bend intrinsic frequencies are 3878 and 1812  $\text{cm}^{-1}$ , respectively. The normal-coordinate frequencies for the O-H stretches (3813 and 3947  $\text{cm}^{-1}$ ) bracket the corresponding intrinsic frequency. Table II contains the intrinsic and normal-coordinate frequencies for NH<sub>3</sub>. In this case, the set of internal coordinates used in the computation of intrinsic frequencies consisted of the three N-H stretches and the three H-N-H bends. The intrinsic frequency for the N-H stretches (3749  $\text{cm}^{-1}$ ) lies between the corresponding normal-coordinate frequencies of 3644 and 3800  $\text{cm}^{-1}$ . Analogous comments apply to the H-N-H bend.

**CH<sub>4</sub>.** The computation of intrinsic frequencies is somewhat more complicated when redundant coordinates are present.<sup>5</sup> Since there are five atoms in methane, we specify nine internal coordinates (four C-H stretches and five of the six H-C-H bends.) The four intrinsic frequencies corresponding to the C-H stretches are all 3261  $\text{cm}^{-1}$ . However, since all H-C-H bends are not included, one obtains intrinsic frequencies of 1629  $\text{cm}^{-1}$  for four of the bends and 1509  $\text{cm}^{-1}$  for the remaining bend. This suggests that inclusion of the sixth (redundant) H-C-H bend in the analysis is required to properly account for the symmetry of the H-C-H bending frequencies. When this is done, the intrinsic frequencies for the four C-H stretches remain at 3261  $\text{cm}^{-1}$ , and the intrinsic frequencies for the six H-C-H bends are all 1466  $\text{cm}^{-1}$  (see Table III). Note that the H-C-H frequency obtained when all six bends are included in the analysis is smaller than the average of the five original frequencies, because each normal coordinate is distributed over a larger number of internal coordinates (six rather than five, since there is little stretch-bend mixing.) An individual internal coordinate thus has a smaller contribution to each normal mode and therefore has a smaller intrinsic frequency. This can be corrected as follows: Since  $\sum_m \sum_n P_{mn}^i = 1$ , regardless of the number of internal coordinates used in the analysis, and since the only elements of  $P_{mn}^i$  that change significantly upon inclusion of the redundant coordinate are for  $r_m, r_n$  equal to one of the H-C-H bends, we have the following approximate relationship:

$$\nu_{\text{rms}} = (j/k)^{1/2} \nu_{\text{bend}} \quad (20)$$

In eq 20,  $j$  ( $k$ ) is the number of H-C-H bends when redundant bends are (not) used,  $\nu_{\text{bend}}$  is the intrinsic frequency for the H-C-H bend when the redundancy is included in the analysis, and  $\nu_{\text{rms}}$  is the root mean square average of the intrinsic bending frequencies when the redundancy is not included. (Equation 20 is not valid when there is more than one kind of redundant internal coordinate

present and/or there is significant mixing of redundant coordinates with nonredundant ones. For example, both of these complications are present in benzene, which has redundant C-C-C and C-C-H angle bends, as well as strong mixing of the C-C stretches and C-C-C bends.)

Also appearing in Tables I-III are the diagonal elements of the  $P^i$  matrices. For H<sub>2</sub>O (Table I), note that the normal mode with a frequency of 1799  $\text{cm}^{-1}$  is dominated by the HOH bending coordinate; that is, the only  $P_{mm}^i$  significantly different from zero is the one corresponding to this particular internal coordinate. Likewise, the two normal modes with frequencies of 3813 and 3947  $\text{cm}^{-1}$  have contributions only from the O-H stretches. Similar comments apply for ammonia (Table II) and methane (Table III). Thus, the  $P_{mn}^i$  are useful in determining qualitative descriptions<sup>12</sup> of normal-coordinate displacements.

**General Treatment of Redundant Coordinates.** When  $m$  redundant coordinates are included in the analysis, the  $G$  matrix in eq 14 is singular. Consequently,  $G$  will have  $m$  zero eigenvalues when it is diagonalized. Under these circumstances, the calculation of  $G^{-1}$  is carried out as indicated in eq 17b except that those values of  $n$  for which  $e_n$  is zero are excluded from the summation.<sup>5,14</sup> For convenience, we will still identify this matrix as  $G^{-1}$ , although strictly speaking the inverse of  $G$  does not exist.

We now address the problem of systematically determining the appropriate number of internal coordinates (i.e., the value of  $S$ ) as well as which internal coordinates to use in this analysis. The usual procedure<sup>5</sup> is to use  $S = 3N - 6$  internal coordinates which are "complete."<sup>15</sup> While the present vibrational analysis can be performed by using such a set of internal coordinates, there is no guarantee (as shown above for methane) that symmetrically equivalent internal coordinates will have identical intrinsic frequencies. In order to ensure that symmetrically equivalent internal coordinates describing angle bends have identical intrinsic frequencies, it is necessary to include all of the symmetry-equivalent counterparts of a given bending coordinate in the analysis. This requires in some instances that redundant coordinates<sup>5</sup> be used, with  $S > 3N - 6$ . The chosen set of internal coordinates must be "complete"<sup>15</sup> in the sense that all vibrational degrees of freedom must be described. For example, in methane it would be improper to use the set of internals consisting of the six H-C-H angle bends and the four H-C-H-H torsion angles, since the distances of the hydrogen atoms from the carbon atom are undetermined. The presence of a noncomplete set of internal coordinates is easily detected by transforming the Cartesian force constant matrix  $\mathbf{f}$  to  $\mathbf{F}$  according to eq 5a, and then performing the reverse transformation (5b) to regain  $\mathbf{f}$ . If the set of internal coordinates is complete, the doubly transformed matrix will equal the original  $\mathbf{f}$ . Conversely, if the set of internal coordinates is not complete, the double transformation will produce a matrix different from the original  $\mathbf{f}$  with a number of zero eigenvalues equal to the number of undetermined vibrational degrees of freedom plus six.

Next consider cyclopropane. The set of internal coordinates consisting of the three C-C stretches, six C-H stretches, and 12 C-C-H bends is complete with no redundant coordinates and also ensures that symmetrically equivalent internal coordinates will have equal intrinsic frequencies (1045, 3363, and 1285  $\text{cm}^{-1}$ , respectively.) If one of the C-C-H bends is replaced by a H-C-H bend, the set of internals is still complete. However, one obtains three distinct C-C stretch intrinsic frequencies (1037, 1043, and 1046  $\text{cm}^{-1}$ ) and four different frequencies for the 11 equivalent C-C-H bends (1109, 1143, 1199, and 1285  $\text{cm}^{-1}$ ).

While care must be taken to include all symmetry-equivalent angles, one must not use more internal coordinates than are necessary to meet the requirement of completeness, to avoid an over-determined set. If in addition to the three C-C stretches, six C-H stretches, and 12 C-C-H bends of cyclopropane, the three C-C-C angles are also included in the vibrational analysis scheme, the symmetry of the intrinsic frequencies is lost, and one obtains intrinsic frequencies of 948, 975, and 1004  $\text{cm}^{-1}$  for the three C-C

(14) Kuczera, K.; Czerminski, R. *THEOCHEM* 1983, 105, 269-280.

(15) Decius, J. C. *J. Chem. Phys.* 1949, 17, 1315-1318.

TABLE III: Harmonic and Intrinsic Frequencies of Methane<sup>a</sup>

| Harmonic Frequencies  |                |   |       |       |       |       |       |       |       |       |
|---|----------------|---|-------|-------|-------|-------|-------|-------|-------|-------|
| freq  |                | normal mode description                                 |       |       |       |       |       |       |       |       |
| 1520 (3)  |                | H-C-H bend  |       |       |       |       |       |       |       |       |
| 1740 (2)  |                | H-C-H bend  |       |       |       |       |       |       |       |       |
| 3187  |                | C-H stretch   |       |       |       |       |       |       |       |       |
| 3280 (3)  |                | C-H stretch   |       |       |       |       |       |       |       |       |
| Diagonal Elements of the Vibrational Density Matrices ( $\mathbf{P}^i$ ) <sup>b</sup> |                |   |       |       |       |       |       |       |       |       |
| internal coord  | intrinsic freq | diagonal elements at the following harmonic frequencies |       |       |       |       |       |       |       |       |
|   |                | 1520  | 1520  | 1520  | 1740  | 1740  | 3187  | 3280  | 3280  | 3280  |
| H-C-H bend  | 1466           | -0.41   | 0.00  | 0.35  | 0.00  | 0.49  | 0.00  | 0.00  | 0.05  | 0.00  |
| H-C-H bend  | 1466           | -0.25   | 0.38  | -0.29 | 0.42  | -0.24 | 0.00  | -0.04 | 0.00  | -0.04 |
| H-C-H bend  | 1466           | 0.25  | 0.38  | 0.29  | -0.42 | -0.24 | 0.00  | -0.04 | 0.00  | 0.04  |
| H-C-H bend  | 1466           | -0.25   | -0.38 | -0.29 | -0.42 | -0.24 | 0.00  | 0.04  | 0.00  | -0.04 |
| H-C-H bend  | 1466           | 0.25  | -0.38 | 0.29  | 0.42  | -0.24 | 0.00  | 0.04  | 0.00  | 0.04  |
| H-C-H bend  | 1466           | 0.41  | 0.00  | -0.35 | 0.00  | 0.49  | 0.00  | 0.00  | -0.05 | 0.00  |
| C-H stretch   | 3261           | 0.02  | -0.03 | -0.01 | 0.00  | 0.00  | -0.50 | 0.74  | -0.52 | 0.01  |
| C-H stretch   | 3261           | 0.02  | 0.03  | -0.01 | 0.00  | 0.00  | -0.50 | -0.74 | -0.52 | 0.01  |
| C-H stretch   | 3261           | 0.00  | 0.00  | 0.04  | 0.00  | 0.00  | -0.50 | 0.00  | 0.54  | 0.73  |
| C-H stretch   | 3261           | -0.04   | 0.00  | -0.01 | 0.00  | 0.00  | -0.50 | 0.00  | 0.51  | -0.75 |

<sup>a</sup>In  $\text{cm}^{-1}$ . The elements of the  $\mathbf{P}^i$  matrices are unitless. The degeneracies of the harmonic frequencies are indicated in parentheses. <sup>b</sup>See text.

stretches and two distinct intrinsic frequencies for the C-C-C bends ( $366$  and  $393 \text{ cm}^{-1}$ .) Thus, the minimum number of coordinates satisfying the symmetry and completeness criteria must be used.

Now, consider molecules in which one or more torsion angles are necessary to completely specify the structure. For example, for the ethane molecule it is necessary to specify one of the H-C-C-H torsion angles (or appropriate nonbonded distances) in order to establish the relative orientations of the two methyl groups. When torsions are used to achieve completeness, the minimum number necessary must be used (see Appendix).

The above empirical rules for the computation of symmetric intrinsic frequencies can be summarized as follows:

- (1) The chosen set of internal coordinates must be complete (this requires a minimum of  $3N - 6$  coordinates).
- (2) All symmetry-equivalent counterparts of a given bending coordinate must be included.
- (3) The minimum number of torsion angles sufficient to satisfy condition (1) must be used.
- (4) The torsion angles used must be defined by symmetry-equivalent atoms, if present.

Rules 3 and 4 are discussed further in the Appendix. If condition (2) or (4) is not satisfied, then symmetry-equivalent internal coordinates will not consistently have identical intrinsic frequencies.

Generally the choice of internal coordinates for a given molecule is not unique, with the implication that the vibrational density matrices and intrinsic frequencies are non-unique as well. However, a certain subset of internal coordinates will be common to all complete sets (e.g., the bond stretches). Therefore, it is of interest to compare the intrinsic frequencies of the internal coordinates within this subset, computed by using each complete set. We have generally observed that the intrinsic frequencies do not change very much (less than  $10 \text{ cm}^{-1}$ ). This is especially true for the bond stretches. For examples of such a comparison, see the Appendix and Tables XI and XII.

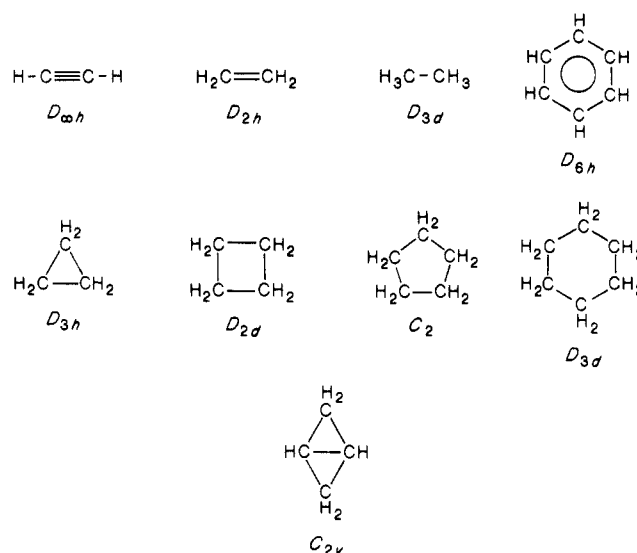
Strictly speaking, intrinsic frequencies of bond stretches are indicators of relative bond strengths only for a given bond type. Intrinsic force constants, on the other hand, generally serve as a measure of relative bond strengths, irrespective of the type of bond. However, the computation of intrinsic force constants  $k_n$  from intrinsic frequencies is straightforward, as shown in eq 21, where  $\mu$  is the reduced mass and  $\nu_n$  is the intrinsic frequency.

$$k_n = \mu(2\pi\nu_n)^2 \quad (21)$$

### III. Results and Discussion

**Structures.** The 3-21G structures for all molecules considered in this work have appeared elsewhere<sup>16,17</sup> and so will not be given

CHART I



here. The systems in Chart I have been subjected to the vibrational analysis scheme outlined in section II.

**Hydrocarbons.** Tables IV and V summarize the harmonic and intrinsic frequencies of ethyne, ethene, ethane, and benzene. The discussion here will focus on the C-C and C-H intrinsic bond stretch frequencies. In the series ethyne  $\rightarrow$  ethene  $\rightarrow$  ethane, the intrinsic frequencies for the C-C stretch ( $2414 > 1759 > 998 \text{ cm}^{-1}$ ) are consistent with the decreasing strength of the C-C bond in these three compounds. In benzene, the formal C-C bond order is 1.5, and therefore a C-C bond strength between those of ethene and ethane is anticipated. The intrinsic C-C stretching frequency for benzene,  $1334 \text{ cm}^{-1}$ , falls between the corresponding intrinsic frequencies for ethene and ethane, and therefore is consistent with the expected relative bond strength. (Note that an analogous comparison of normal-coordinate C-C stretching frequencies for these four compounds is hampered by the coupling of the C-C stretches with C-C-H bends in benzene.)

Similar comments apply to the C-H stretching frequencies. In the series ethyne  $\rightarrow$  ethene  $\rightarrow$  ethane, the carbon atoms are formally  $\text{sp}$ ,  $\text{sp}^2$ , and  $\text{sp}^3$  hybridized, respectively. Since the

(16) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213.

(17) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352-358.

TABLE IV: Harmonic and Intrinsic Frequencies of Ethyne, Ethene, and Ethane<sup>a</sup>

| molecule                         | harmonic freq | description                  | intrinsic freq | internal coord               |
|----------------------------------|---------------|------------------------------|----------------|------------------------------|
| HC≡CH                            | 794 (2)       | C-C-H bend                   | 839 (4)        | C-C-H bend                   |
|                                  | 882 (2)       | C-C-H bend                   | 2414           | C-C stretch                  |
|                                  | 2247          | C-C stretch                  | 3610 (2)       | C-H stretch                  |
|                                  | 3607          | C-H stretch                  |                |                              |
|                                  | 3719          | C-H stretch                  |                |                              |
| H <sub>2</sub> C=CH <sub>2</sub> | 944           | C-C-H bend                   | 981 (2)        | H-C-C-H torsion <sup>c</sup> |
|                                  | 1115          | H-H-C-H op bend <sup>b</sup> | 1004 (2)       | H-C-C-H torsion <sup>d</sup> |
|                                  | 1157          | H-H-C-H op bend <sup>b</sup> | 1432 (4)       | C-C-H bend                   |
|                                  | 1166          | H-C-C-H torsion              | 1759           | C-C stretch                  |
|                                  | 1388          | C-C-H bend                   | 3348 (4)       | C-H stretch                  |
|                                  | 1522          | C-C stretch, C-C-H bend      |                |                              |
|                                  | 1640          | C-C-H bend                   |                |                              |
|                                  | 1842          | C-C stretch                  |                |                              |
|                                  | 3305          | C-H stretch                  |                |                              |
|                                  | 3326          | C-H stretch                  |                |                              |
|                                  | 3370          | C-H stretch                  |                |                              |
|                                  | 3402          | C-H stretch                  |                |                              |
| H <sub>3</sub> C-CH <sub>3</sub> | 307           | H-C-C-H torsion              | 307            | H-C-C-H torsion              |
|                                  | 920 (2)       | C-C-H bend                   | 998            | C-C stretch                  |
|                                  | 1005          | C-C stretch                  | 1159 (6)       | C-C-H bend                   |
|                                  | 1350 (2)      | C-C-H bend                   | 1496 (6)       | H-C-H bend                   |
|                                  | 1572          | H-C-H bend, C-C-H bend       | 3240 (6)       | C-H stretch                  |
|                                  | 1580          | H-C-H bend, C-C-H bend       |                |                              |
|                                  | 1677 (2)      | H-C-H bend                   |                |                              |
|                                  | 1678 (2)      | H-C-H bend                   |                |                              |
|                                  | 3198          | C-H stretch                  |                |                              |
|                                  | 3202          | C-H stretch                  |                |                              |
|                                  | 3242 (2)      | C-H stretch                  |                |                              |
|                                  | 3269 (2)      | C-H stretch                  |                |                              |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses. <sup>b</sup> op bend denotes an out-of-plane torsion. <sup>c</sup> *trans* torsion angle. <sup>d</sup> *cis* torsion angle.

TABLE V: Harmonic and Intrinsic Frequencies of Benzene<sup>a</sup>

| harmonic freq | description                                   | intrinsic freq | internal coord               |
|---------------|---|----------------|------------------------------|
| 466 (2)       | C-C-C torsion                                 | 455 (3)        | C-C-C-C torsion              |
| 698 (2)       | C-C-H bend, C-C-C bend                        | 616 (6)        | C-C-C bend                   |
| 784           | C-C-C-H op bend <sup>b</sup>                  | 1091 (12)      | C-C-H bend                   |
| 995           | C-C-C-H op bend <sup>b</sup>                  | 1095 (6)       | C-C-C-H op bend <sup>b</sup> |
| 1078          | C-C stretch                                   | 1334 (6)       | C-C stretch                  |
| 1137 (2)      | C-C stretch                                   | 3360 (6)       | C-H stretch                  |
| 1148          | C-C-C bend, C-C-H bend                        |                |                              |
| 1156 (2)      | C-C-C-H op bend <sup>b</sup>                  |                |                              |
| 1200          | C-C-C-C torsion, C-C-C-H op bend <sup>b</sup> |                |                              |
| 1235          | C-C stretch                                   |                |                              |
| 1323 (2)      | C-C stretch, C-C-H bend                       |                |                              |
| 1366          | C-C stretch, C-C-H bend                       |                |                              |
| 1544          | C-C-H bend                                    |                |                              |
| 1658 (2)      | C-C stretch, C-C-H bend                       |                |                              |
| 1764 (2)      | C-C stretch                                   |                |                              |
| 3345          | C-H stretch                                   |                |                              |
| 3355 (2)      | C-H stretch                                   |                |                              |
| 3373 (2)      | C-H stretch                                   |                |                              |
| 3388          | C-H stretch                                   |                |                              |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses. <sup>b</sup> op bend denotes an out-of-plane torsion.

percentage of s character in the hybrid bonds decreases in this sequence, one expects a parallel decrease in the C-H bond strength and therefore a concomitant decrease in the C-H stretching frequency. This is in fact observed for the intrinsic C-H stretching frequencies, which are 3610, 3348, and 3240 cm<sup>-1</sup>, respectively. Since the carbon atoms in benzene are formally sp<sup>2</sup> hybridized, the C-H bonds should exhibit similar bond strengths and stretching frequencies to those in ethene. Indeed, the C-H stretching intrinsic frequency of 3360 cm<sup>-1</sup> is very close to the corresponding frequency of 3348 cm<sup>-1</sup> for ethene.

**Cycloalkanes.** Tables VI-IX summarize the normal-coordinate frequencies and the intrinsic frequencies for cyclopropane, cyclobutane, cyclopentane, and cyclohexane. (The complete nor-

TABLE VI: Harmonic and Intrinsic Frequencies of Cyclopropane<sup>a</sup>

| harmonic freq     | intrinsic freq | internal coord |
|-------------------|----------------|----------------|
| 834 (2)           | 1045 (3)       | C-C stretch    |
| 910 (2)           | 1285 (12)      | H-C-C bend     |
| 920               | 3363 (6)       | C-H stretch    |
| 1208 (2)          |                |                |
| 1216 <sup>b</sup> |                |                |
| 1269              |                |                |
| 1272              |                |                |
| 1327 (2)          |                |                |
| 1622 (2)          |                |                |
| 1656              |                |                |
| 3319 (2)          |                |                |
| 3332              |                |                |
| 3397 (2)          |                |                |
| 3421              |                |                |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses. <sup>b</sup> This mode is a C-C stretch. See ref 16 for complete normal-coordinate descriptions.

mal-coordinate descriptions for these ring systems have appeared elsewhere<sup>17</sup> and so are not given in the tables.) The discussion here will deal only with the intrinsic frequencies of the C-C and C-H stretches.

The C-C stretching intrinsic frequency of cyclopropane is 1045 cm<sup>-1</sup> (see Table VI). The analogous quantity for cyclobutane is 950 cm<sup>-1</sup> (Table VII). Cyclopentane has three C-C stretching intrinsic frequencies (932, 957, and 987 cm<sup>-1</sup>) since this molecule has three symmetry-unique C-C bonds (see Table VIII). It is seen from Table IX that cyclohexane has an intrinsic C-C stretching frequency of 999 cm<sup>-1</sup>. These values are perhaps best compared with the C-C stretch intrinsic frequency for the central bond in *n*-butane, which is 997 cm<sup>-1</sup> (not given in the tables.) This is chosen as a reference because it is the simplest unstrained single bond between two secondary carbon atoms. The C-C intrinsic frequency for cyclopropane is larger (1045 cm<sup>-1</sup>) than that of the reference intrinsic frequency, while the C-C stretch intrinsic frequencies of the remaining cycloalkanes are less than or about equal to the reference value. This is consistent with the fact that

TABLE VII: Harmonic and Intrinsic Frequencies of Cyclobutane<sup>a</sup>

| harmonic freq        | intrinsic freq | internal coord |
|----------------------|----------------|----------------|
| 205                  | 602 (4)        | C-C-C bend     |
| 707                  | 950 (4)        | C-C stretch    |
| 819 (2)              | 1319 (8)       | H-C-C bend     |
| 938 (2) <sup>b</sup> | 1355 (8)       | H-C-C bend     |
| 965 <sup>b</sup>     | 3196 (4)       | C-H stretch    |
| 965 <sup>b</sup>     | 3274 (4)       | C-H stretch    |
| 1021 <sup>b</sup>    |                |                |
| 1097                 |                |                |
| 1270                 |                |                |
| 1286                 |                |                |
| 1366 (2)             |                |                |
| 1402                 |                |                |
| 1418                 |                |                |
| 1431 (2)             |                |                |
| 1637 (2)             |                |                |
| 1639                 |                |                |
| 1673                 |                |                |
| 3185                 |                |                |
| 3186 (2)             |                |                |
| 3192                 |                |                |
| 3278                 |                |                |
| 3281 (2)             |                |                |
| 3292                 |                |                |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses.

<sup>b</sup> This mode is a combination of a C-C stretch and a C-C-C bend. See ref 16 for complete normal-coordinate descriptions.

cyclopropane has the shortest C-C *bent* bond length,<sup>17</sup> and therefore presumably the stiffest bond, of all the C-C bonds in these cycloalkanes. However, all of the intrinsic C-C frequencies are quite similar.

The C-H stretches of the cycloalkanes are considered next. In cyclopropane, the intrinsic C-H frequency is 3363 cm<sup>-1</sup>. Because cyclobutane has two symmetry-unique C-H bonds, it has distinct C-H intrinsic frequencies of 3196 and 3274 cm<sup>-1</sup>. Similarly, cyclopentane has five C-H intrinsic frequencies of 3224, 3234, 3250, 3251, and 3254 cm<sup>-1</sup>. Cyclohexane has two unique C-H bonds and therefore has C-H intrinsic frequencies of 3207 and 3220 cm<sup>-1</sup>. As in the case of the C-C stretch, we choose the intrinsic frequency of the C-H stretch of the methylene carbon in *n*-butane as our reference value (3215 cm<sup>-1</sup>). The C-H intrinsic frequency of cyclopropane is over 100 cm<sup>-1</sup> larger than this reference value; the remaining C-H intrinsic frequencies of the other rings are all within 60 cm<sup>-1</sup> of the reference. The larger C-H stretch frequencies for cyclopropane are consistent with the fact that the C-H bonds in this compounds are the shortest of all the C-H bonds in the ring systems considered here.<sup>17</sup>

**Bicyclobutane.** As a somewhat more complex example, we have computed intrinsic frequencies for bicyclobutane (Table X). (The complete normal-coordinate descriptions have appeared elsewhere<sup>18</sup> and so will not be repeated here.) In a forthcoming paper,<sup>19</sup> we will present the intrinsic frequencies for all nine silicon-substituted bicyclobutanes Si<sub>n</sub>C<sub>4-n</sub>H<sub>6</sub>, *n* = 0-4. As with the hydrocarbons and cycloalkanes, the discussion here will focus on the intrinsic C-C and C-H stretching frequencies.

The heavy-atom framework of bicyclobutane consists of a C-C bridge bond and four symmetrically equivalent C-C peripheral bonds. The intrinsic frequencies for the peripheral and bridge bond stretches are 982 and 1227 cm<sup>-1</sup>, respectively, and thus indicate that the bridge bond is stiffer than the peripheral bonds. These results are also consistent with the fact that the bridge bond has a shorter *bent* bond length than the peripheral C-C bonds.<sup>20</sup>

Since there are two symmetry-unique peripheral C-H bonds, two distinct intrinsic frequencies of 3304 and 3345 cm<sup>-1</sup> are obtained. These values are smaller than those for the bridge C-H

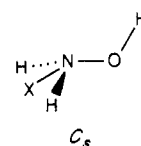
TABLE VIII: Harmonic and Intrinsic Frequencies of Cyclopentane<sup>a</sup>

| harmonic freq     | intrinsic freq | internal coord  |
|-------------------|----------------|-----------------|
| 0 <sup>b</sup>    | 356 (2)        | C-C-C-C torsion |
| 277               | 913 (2)        | C-C-C bend      |
| 595               | 957 (2)        | C-C stretch     |
| 674               | 1013           | C-C stretch     |
| 829               | 1032 (2)       | C-C stretch     |
| 886               | 1344 (2)       | H-C-C bend      |
| 908               | 1351 (2)       | H-C-C bend      |
| 930 <sup>c</sup>  | 1352 (2)       | H-C-C bend      |
| 937 <sup>c</sup>  | 1361 (2)       | H-C-C bend      |
| 942 <sup>c</sup>  | 1365 (2)       | H-C-C bend      |
| 1075              | 1378 (2)       | H-C-C bend      |
| 1091 <sup>c</sup> | 1381 (2)       | H-C-C bend      |
| 1107 <sup>c</sup> | 1381 (2)       | H-C-C bend      |
| 1113              | 1384 (2)       | H-C-C bend      |
| 1292 <sup>c</sup> | 1389 (2)       | H-C-C bend      |
| 1335              | 3224 (2)       | C-H stretch     |
| 1349              | 3234 (2)       | C-H stretch     |
| 1367              | 3250 (2)       | C-H stretch     |
| 1419              | 3251 (2)       | C-H stretch     |
| 1457              | 3254 (2)       | C-H stretch     |
| 1471              |                |                 |
| 1475              |                |                 |
| 1489              |                |                 |
| 1489              |                |                 |
| 1645              |                |                 |
| 1651              |                |                 |
| 1655              |                |                 |
| 1657              |                |                 |
| 1682              |                |                 |
| 3209              |                |                 |
| 3210              |                |                 |
| 3216              |                |                 |
| 3218              |                |                 |
| 3236              |                |                 |
| 3250              |                |                 |
| 3260              |                |                 |
| 3266              |                |                 |
| 3268              |                |                 |
| 3286              |                |                 |

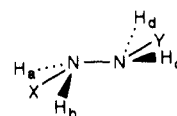
<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses.

<sup>b</sup> This mode is a free pseudorotation motion. <sup>c</sup> This mode is a combination of a C-C stretch and a C-C-C bend. See ref 16 for complete normal-coordinate descriptions.

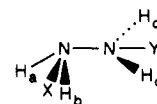
## CHART II



## CHART III



## CHART IV



stretches, which have an intrinsic frequency of 3468 cm<sup>-1</sup>. The higher intrinsic frequency for the bridge C-H bonds is consistent with the fact that these bonds are shorter than the peripheral C-H bonds.<sup>20</sup>

## IV. Conclusions

It has been demonstrated that intrinsic frequencies can be of significant utility in the characterization of bonds via computation

(18) Wiberg, K. B.; Peters, K. S. *Spectrochim. Acta, Part A* 1977, 33A, 261-271.

(19) Boatz, J. A.; Gordon, M. S., to be submitted for publication.

(20) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* 1988, 92, 3037-3042.

TABLE IX: Harmonic and Intrinsic Frequencies of Cyclohexane<sup>a</sup>

| harmonic freq         | intrinsic freq | internal coord  |
|-----------------------|----------------|-----------------|
| 248 (2)               | 282 (3)        | C-C-C-C torsion |
| 407                   | 650 (6)        | C-C-C bend      |
| 464 (2)               | 999 (6)        | C-C stretch     |
| 572                   | 1378 (12)      | C-C-H bend      |
| 828                   | 1390 (12)      | C-C-H bend      |
| 869 (2)               | 3207 (6)       | C-H stretch     |
| 897 (2)               | 3220 (6)       | C-H stretch     |
| 1011 (2)              |                |                 |
| 1098 (2) <sup>b</sup> |                |                 |
| 1137                  |                |                 |
| 1144                  |                |                 |
| 1202                  |                |                 |
| 1259                  |                |                 |
| 1291 <sup>b</sup>     |                |                 |
| 1417 (2) <sup>b</sup> |                |                 |
| 1420 (2) <sup>b</sup> |                |                 |
| 1500 <sup>b</sup>     |                |                 |
| 1505 <sup>b</sup>     |                |                 |
| 1511                  |                |                 |
| 1525 (2)              |                |                 |
| 1650 (2)              |                |                 |
| 1652 (2)              |                |                 |
| 1664                  |                |                 |
| 1672                  |                |                 |
| 3188                  |                |                 |
| 3189 (2)              |                |                 |
| 3190 (2)              |                |                 |
| 3193                  |                |                 |
| 3226 (2)              |                |                 |
| 3231                  |                |                 |
| 3234 (2)              |                |                 |
| 3248                  |                |                 |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses.<sup>b</sup> This mode is a combination of a C-C stretch and a C-C-C bend. See ref 16 for complete normal-coordinate descriptions.TABLE X: Harmonic and Intrinsic Frequencies of Bicyclobutane<sup>a</sup>

| harmonic freq     | intrinsic freq | internal coord <sup>b</sup>  |
|-------------------|----------------|--|
| 507               | 982 (4)        | C <sub>b</sub> -C <sub>p</sub> stretch                                 |
| 789 <sup>c</sup>  | 1010           | C <sub>p</sub> -C <sub>b</sub> -C <sub>b</sub> -C <sub>p</sub> torsion |
| 861 <sup>c</sup>  | 1127 (4)       | C <sub>p</sub> -C <sub>b</sub> -H <sub>b</sub> bend                    |
| 900 <sup>d</sup>  | 1227           | C <sub>b</sub> -C <sub>b</sub> stretch                                 |
| 943 <sup>d</sup>  | 1307 (4)       | C <sub>b</sub> -C <sub>p</sub> -H <sub>p</sub> bend                    |
| 1020              | 1315 (4)       | C <sub>b</sub> -C <sub>p</sub> -H <sub>p</sub> bend                    |
| 1033              | 3304 (2)       | C <sub>p</sub> -H <sub>p</sub> stretch                                 |
| 1133 <sup>c</sup> | 3345 (2)       | C <sub>p</sub> -H <sub>p</sub> stretch                                 |
| 1139              | 3468 (2)       | C <sub>b</sub> -H <sub>b</sub> stretch                                 |
| 1184 <sup>d</sup> |                |  |
| 1217              |                |  |
| 1265              |                |  |
| 1290              |                |  |
| 1310              |                |  |
| 1346 <sup>d</sup> |                |  |
| 1385              |                |  |
| 1636              |                |  |
| 1667              |                |  |
| 3278 <sup>e</sup> |                |  |
| 3280 <sup>e</sup> |                |  |
| 3369 <sup>e</sup> |                |  |
| 3370 <sup>e</sup> |                |  |
| 3468 <sup>f</sup> |                |  |
| 3487 <sup>f</sup> |                |  |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses.<sup>b</sup> The subscripts b and p indicate bridge and peripheral atoms, respectively. <sup>c</sup> This mode is partly composed of a C<sub>p</sub>-C<sub>b</sub> stretch. See ref 17 for complete normal-coordinate descriptions. <sup>d</sup> This mode is partly composed of a C<sub>b</sub>-C<sub>b</sub> stretch. See ref 17 for complete normal-coordinate descriptions. <sup>e</sup> This mode is a C<sub>p</sub>-H<sub>p</sub> stretch. <sup>f</sup> This mode is a C<sub>b</sub>-H<sub>b</sub> stretch.

of harmonic force fields. This is particularly true for those cases in which several internal coordinates are highly coupled in a given normal-coordinate displacement. The vibrational density matrices

TABLE XI: Intrinsic Frequencies of Hydroxylamine<sup>a</sup>

| internal coord               | set A <sup>b</sup> | set B <sup>b</sup> | set C <sup>b</sup> |
|------------------------------|--------------------|--------------------|--------------------|
| N-O stretch                  | 1097               | 1097               | 1097               |
| O-H stretch                  | 3857               | 3857               | 3857               |
| N-H stretch                  | 3654 (2)           | 3654 (2)           | 3654 (2)           |
| H-O-N bend                   | 1460               | 1460               | 1460               |
| H-N-O bend                   | 1394, 1404         | 1466 (2)           | 1399 (2)           |
| H-N-H bend                   | 1707               |                    | 1707               |
| H-N-O-H torsion              | 457                | 1171 (2)           |                    |
| X-N-O-H torsion <sup>b</sup> |                    |                    | 457                |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses.<sup>b</sup> See Appendix.TABLE XII: Intrinsic Frequencies of Hydrazine<sup>a</sup>

| C <sub>2h</sub> (trans) Conformer <sup>b</sup> |                       |                       |                    |  |
|--|-----------------------|-----------------------|--------------------|--|
| internal coord <sup>b</sup>                    | set D <sup>c</sup>    | set E <sup>c</sup>    | set F <sup>c</sup> |  |
| N-N stretch                                    | 1048                  | 1048                  | 1048               |  |
| N-H stretch                                    | 3636 (4)              | 3636 (4)              | 3636 (4)           |  |
| H-N-N bend                                     | 1387 (2),<br>1393 (2) | 1387 (2),<br>1393 (2) | 1390 (4)           |  |
| H-N-H bend                                     | 1728 (2)              | 1728 (2)              | 1728 (2)           |  |
| H <sub>a</sub> -N-N-H <sub>c</sub> torsion     | 145                   |                       |                    |  |
| H <sub>a</sub> -N-N-H <sub>d</sub> torsion     |                       | 145                   |                    |  |
| X-N-N-Y torsion                                |                       |                       | 145                |  |

| C <sub>2</sub> (gauche) Conformer <sup>d</sup>                            |                    |                    |                    |                    |
|---|--------------------|--------------------|--------------------|--------------------|
| internal coord <sup>b</sup>   | set G <sup>c</sup> | set H <sup>c</sup> | set I <sup>c</sup> | set J <sup>c</sup> |
| N-N stretch   | 1099               | 1099               | 1099               | 1099               |
| N-H <sub>a</sub> (H <sub>d</sub> ) stretch                                | 3731 (2)           | 3731 (2)           | 3731 (2)           | 3731 (2)           |
| N-H <sub>b</sub> (H <sub>c</sub> ) stretch                                | 3665 (2)           | 3665 (2)           | 3665 (2)           | 3665 (2)           |
| H <sub>a</sub> (H <sub>d</sub> )-N-N bend                                 | 1356 (2)           | 1346 (2)           | 1351 (2)           | 1346, 1356         |
| H <sub>b</sub> (H <sub>c</sub> )-N-N bend                                 | 1346 (2)           | 1342 (2)           | 1344 (2)           | 1342, 1346         |
| H <sub>a</sub> -N-H <sub>b</sub> (H <sub>c</sub> -N-H <sub>d</sub> ) bend | 1625 (2)           | 1622 (2)           | 1624 (2)           | 1622, 1625         |
| H <sub>a</sub> -N-N-H <sub>d</sub> torsion                                | 442                |                    |                    |                    |
| H <sub>b</sub> -N-N-H <sub>c</sub> torsion                                |                    | 537                |                    |                    |
| X-N-N-Y torsion   |                    |                    | 491                |                    |
| H <sub>a</sub> -N-N-H <sub>c</sub> torsion                                |                    |                    |                    | 491                |

<sup>a</sup> In cm<sup>-1</sup>. The frequency degeneracies are indicated in parentheses.<sup>b</sup> See Chart III. <sup>c</sup> See Appendix. <sup>d</sup> See Chart IV.

P<sub>i</sub> are helpful in providing a qualitative description of normal-coordinate motions in terms of internal coordinates.

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## Appendix

As mentioned in section II, certain criteria must be satisfied if torsion angles are to be included in the set of internal coordinates used for the computation of intrinsic frequencies. These criteria are illustrated by first considering the molecule hydroxylamine (NH<sub>2</sub>OH) shown in Chart II. (X denotes the point midway between the two amine hydrogens.) Consider three sets of internal coordinates, all of which are complete, satisfy the symmetry requirement for angle bends, and have  $S = 3N - 6 = 9$ . These three sets, designated as A, B, and C, have the four bond stretches, the H-O-N bend, and the two H-N-O bends in common. Set A also contains the H-N-H bend and one of the two symmetrically equivalent H-N-O-H torsions, and set B is completed with both H-N-O-H torsions. Set C includes the H-N-H angle and the X-N-O-H torsion. The intrinsic frequencies obtained by using these three sets of internal coordinates are given in Table XI.

When the vibrational analysis is performed with the internal coordinates in set A, one obtains different intrinsic frequencies

(1394 and 1404  $\text{cm}^{-1}$ ) for the identical H-N-O angle bends, because the use of one H-N-O-H torsion does not treat the two bends equivalently. Replacement of the H-N-H bend with the second symmetry-equivalent H-N-O-H torsion (set B) yields equal intrinsic frequencies for the two H-N-O bends. However, the intrinsic frequency for the torsions is unusually large (1171  $\text{cm}^{-1}$ ) compared to the corresponding normal-coordinate torsion frequency of 450  $\text{cm}^{-1}$  (not given in Table XI). Set B thus illustrates the result of not choosing the minimal number of torsions in obtaining a vibrationally complete set of internal coordinates. Set C accounts for the symmetry of the H-N-O bends and yields a physically reasonable intrinsic frequency for the torsion (457  $\text{cm}^{-1}$ ) as well.

To further illustrate the importance of symmetry, consider the  $C_{2h}$  (*anti*) conformer of hydrazine,  $\text{N}_2\text{H}_4$ , shown in Chart III. (X and Y are points midway between the hydrogens at each end of the molecule.) In the above chart all four H atoms are symmetrically equivalent. Consider three sets of internal coordinates that are complete, satisfy the symmetry requirements for angle bends, and use the minimal number of coordinates (12). These three sets, denoted as D, E, and F, have the five stretches, the four H-N-N angle bends, and the two H-N-H bends in common. Sets D, E, and F include the  $\text{H}_a\text{-N-N-H}_c$ ,  $\text{H}_a\text{-N-N-H}_d$ , and  $\text{X-N-N-Y}$  torsions, respectively. The intrinsic frequencies obtained by using these three sets are given in Table XII. For set F, symmetry-equivalent internal coordinates have equal intrinsic frequencies, but the same is not true for sets D and E. That set

F properly accounts for the symmetry of hydrazine is a direct result of the symmetrical nature of the X-N-N-Y torsion. Sets D and E, on the other hand, include the  $\text{H}_a\text{-N-N-H}_c$  and  $\text{H}_a\text{-N-N-H}_d$  torsions, respectively, which do not treat all four symmetrically equivalent hydrogen atoms equally.

In the case of the  $C_2$  (*gauche*) conformer of hydrazine, all four hydrogen atoms are no longer equivalent to each other. Rather, only the  $\text{H}_a\text{-H}_d$  and  $\text{H}_b\text{-H}_c$  pairs are equivalent (see Chart IV). Since the  $\text{H}_a\text{-H}_b$  and  $\text{H}_c\text{-H}_d$  pairs are not symmetrically equivalent, the choice of an appropriate torsion angle is more flexible. That is, the  $\text{H}_a\text{-N-N-H}_d$ ,  $\text{H}_b\text{-N-N-H}_c$ , and  $\text{X-N-N-Y}$  torsions (sets G, H, and I, respectively, in Table XII) all properly account for the symmetry of the *gauche* conformer of hydrazine. However, the  $\text{H}_a\text{-N-N-H}_c$  torsion (set J in Table XII) fails in this regard since  $\text{H}_a$  and  $\text{H}_c$  are not equivalent.

The above observations suggest the following guidelines for using torsion angles in computing intrinsic frequencies:

(1) The minimum number of torsions sufficient to attain completeness should be used.

(2) The torsion angles used must treat symmetrically equivalent atoms in an equivalent manner.

**Registry No.**  $\text{H}_2\text{O}$ , 7732-18-5;  $\text{NH}_3$ , 7664-41-7;  $\text{CH}_4$ , 74-82-8;  $\text{CH}\equiv\text{CH}$ , 74-86-2;  $\text{CH}_2=\text{CH}_2$ , 74-85-1;  $\text{CH}_3-\text{CH}_3$ , 74-84-0;  $\text{CH}_2-\text{C}-\text{H}_2-\text{CH}_2$ , 75-19-4;  $\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2$ , 287-23-0;  $\text{CH}_2-(\text{CH}_2)_3-\text{CH}_2$ , 287-92-3;  $\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2$ , 110-82-7; benzene, 71-43-2; bicyclobutane, 157-33-5.

## Phosphorescence of *trans*-Stilbene, Stilbene Derivatives, and Stilbene-like Molecules at 77 K

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For some rigid stilbene analogues and various *trans*-1,2-diarylethylenes, including styrylpyridines, dipyrindylethylenes, and a series of substituted stilbenes, phosphorescence spectra and lifetimes ( $\tau_p$ ) were determined in nonpolar and polar glasses at 77 K, partly in the presence of 2-10% ethyl iodide. The triplet energies range from 52.2 kcal/mol for indeno[2,1-*a*]indene to 45.2 kcal/mol for *trans*-4-nitro-4'-methoxystilbene. The  $\tau_p$  values are in the 10-ms domain, and they are shorter when the internal or external heavy-atom effects are involved. The quantum yield of phosphorescence ( $\Phi_p$ ) of *trans*-4-nitrostilbene and the parent stilbene is  $3 \times 10^{-4}$  and  $\leq 1 \times 10^{-5}$ , respectively. The  $\Phi_p$  values reflect the changes in the quantum yield of intersystem crossing ( $\Phi_{isc}$ ) and the ratio of the rate constants for the radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) triplet decay transitions. These values are of the order of  $k_r = 0.05 \text{ s}^{-1}$  and  $k_{nr} = 100 \text{ s}^{-1}$ , as concluded from the  $\tau_p$ ,  $\Phi_p$ , and  $\Phi_{isc}$  values of 4-aceto-, 4-benzoyl-, and 4-nitrostilbene in several glassy media.

### Introduction

Generally, information about the triplet state of aromatic molecules is easily obtained from the phosphorescence spectra in glassy media.<sup>1</sup> However, phosphorescence is difficult to observe with compounds containing a styrene or stilbene chromophore.<sup>2-4</sup> To the best of our knowledge, only a few studies have been published on the phosphorescence of *trans*-stilbene and stilbene-like compounds.<sup>3-5</sup> Not even for *trans*-4-nitrostilbenes,<sup>6-8</sup> where the

quantum yield of fluorescence ( $\Phi_f$ ) is generally small while that for intersystem crossing is substantial ( $\Phi_{isc}$  equals up to 0.9), has phosphorescence data been reported so far. Saltiel et al. have reported phosphorescence maxima ( $\lambda_{max}$ ) of 580 and 601 nm for *trans*-stilbene and the rigid analogue indeno[2,1-*a*]indene, respectively.<sup>3</sup> The former value is confirmed here, whereas the latter is slightly revised.

The energy of the triplet state ( $E_T$ ) of stilbene has been determined by other methods, such as UV/vis absorption under high pressure of oxygen<sup>9</sup> or in a heavy-atom solvent<sup>10</sup> and by energy-

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