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82

L. A. Carreira, R. C. Lord, and
T. B. Malloy, Jr.
Low-Frequency Vibrations
in Small Ring Molecules

G. O. Sørensen
A New Approach to the Hamiltonian
of Nonrigid Molecules

Large Amplitude Motion in Molecules II

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Large Amplitude Motion in Molecules II

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Contents

Low-Frequency Vibrations in Small Ring Molecules
Lionel A. Carreira, Richard C. Lord, and Thomas B. Malloy, Jr. 1

A New Approach to the Hamiltonian of Nonrigid Molecules
Georg Ole Sørensen 97

Author Index Volumes 26–82 177

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Low-Frequency Vibrations in Small Ring Molecules

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Table of Contents

I Introduction 3

II Experimental Methods 4
- A. Far and Mid Infrared Spectroscopy 4
- B. Raman Spectroscopy 6
- C. Microwave Spectroscopy 7

III Theoretical Basis for Interpretation of the Spectra 9
- A. Introduction 9
- B. The General Hamiltonian 10
- C. One-Dimensional Hamiltonians 16
  - 1 Symmetrical Potential Functions 16
  - 2 Reduced-Mass Calculations 20
  - 3 Asymmetric One-Dimensional Hamiltonians 21
- D. Two-Dimensional Hamiltonians 25
  - 1 Pure Pseudorotation 25
  - 2 Hindered Pseudorotation 29

IV Summary of Results with Examples 30
- A. Molecules Treated by One-Dimensional Hamiltonians 30
  - 1 Symmetric Systems 30
    - a) Four-Membered Rings: Trimethylene Oxide, Trimethylene Sulfide, Methylenecyclobutane, Silacyclobutane, Cyclobutane . 31
    - b) Pseudo Four-Membered Rings: Dihydrofuran, Cyclopentene, Dioxadiene, 1,3-Cyclohexadiene, 1,4-Cyclohexadiene 52

    - 2 Asymmetric Systems: Trimethylene Imine, Dihydropyrrole, Analogs of Bicyclo [3.1.0]-hexane 58
  - B. Molecules Treated by Two-Dimensional Hamiltonians 68
    - 1 Pure Pseudorotation: Cyclopentane 68
    - 2 Hindered Pseudorotation: Tetrahydrofuran, Dioxolane 68
    - 3 Coupled Bending and Twisting Vibrations in Cyclopentanone . . . 70
    - 4 Pseudo Five-Membered Rings: Dioxene 74

V Prospects for Further Studies 79

VI References 91

I Introduction

It is well known that the mean-square amplitude of a molecular vibration in a given quantum state is inversely proportional to the product of the reduced mass and the frequency of the vibration. If it has both a small reduced mass and a frequency that is low because of small force constants, the resultant amplitude of vibration will be large. Among the modes of vibration that have small force constants are the inversion of pyramidal molecules, torsion about single bonds, bending of quasi-linear molecules, and the vibrations of ring molecules parallel to the axis of the ring. All but the last are discussed in other chapters of this volume; here we will be concerned with small ring molecules composed of light atoms, whose ring puckering vibrations have large amplitudes and hence cannot be treated by the addition of small terms of higher order to a quadratic potential system.

Transitions between the vibrational states of low-frequency vibrations are directly observable in the far infrared absorption spectrum or as low-frequency Raman shifts. The Boltzmann factors of these states are relatively large at room temperatures, even for fairly high values of the vibrational quantum number v. In addition the transition moments are substantially larger than those of a harmonic oscillator for the same v's, and thus it is often possible to observe a long progression of transitions either in infrared absorption or the Raman effect or both. When such observations extend to levels above a barrier to inversion, the potential-energy curve or surface can be mapped with accuracy to points higher than the barrier and the barrier determined with an accuracy corresponding to that of the spectroscopic measurements.

Since the potential-energy function for low-frequency vibrations involves weak force constants, the function is sensitive to intermolecular forces, which can reach comparable magnitudes to the intramolecular ones at short intermolecular distances. Thus in the liquid states the intramolecular levels are so seriously broadened as to make them difficult to observe, while in crystals the inversion barriers are drastically altered. Thus the most meaningful spectra are necessarily observed in the gas phase, and this delayed the development of the subject until suitable far infrared, laser Raman and microwave techniques were developed, as summarized below.

The experimental observation of ring-puckering motions was preceded by some insightful theoretical suggestions. Bell1) recognized that the ring-puckering vibration in cyclobutane should have a large quartic term in its potential function, and Rathjens et al.2) proposed a double-minimum potential for this molecule which predicted a highly anharmonic set of levels for the ring puckering. Pitzer and co-workers3) also were led by studies of the heat capacity and entropy of cyclopentane to postulate an unusual relationship between the two components of the approximately degenerate ring-puckering vibrations in that molecule. This relationship they termed "pseudo-rotation" because the successive displacements in the vibration give the appearance of a rotation of the distorted molecule.

The first direct spectroscopic observation of the highly anharmonic nature of ring puckering in a small ring molecule was made by Danti4), who found part of the progression for oxetane at 90–140 cm^{-1} in far infrared absorption. This work was confirmed by the spectrum of oxetane-d_6[5], and the nature of the isotopic shifts as well as the absolute values of the frequencies made it clear that the potential function is nearly a pure quartic. Pseudorotation was not observed first in cyclopentane but in the analog oxolane (tetrahydrofuran)[6]. In the latter molecule there is a small barrier to pseudorotation, as is discussed in Section IV. B., below. Quantitative measurement of the pseudorotational energy levels in cyclopentane, which confirmed the postulates of Pitzer et al.[3], was first made by means of combination bands in the mid-infrared by Durig and Wertz[7].

Since this early work the theoretical and experimental aspects of low-frequency ring vibrations have grown rapidly. In the sections below we sketch briefly the experimental methods developed to investigate ring molecules (Section II), review the theoretical basis for the interpretation of the spectroscopic data (Section III), and give an illustrative survey of the applications of the theory to the special cases of individual molecules (Section IV).

II Experimental Methods

A. Far and Mid Infrared Spectroscopy

Since the early far infrared work on ring molecules[4, 5] there has been a considerable improvement in instrumentation, first in conventional grating spectrometers[8] and

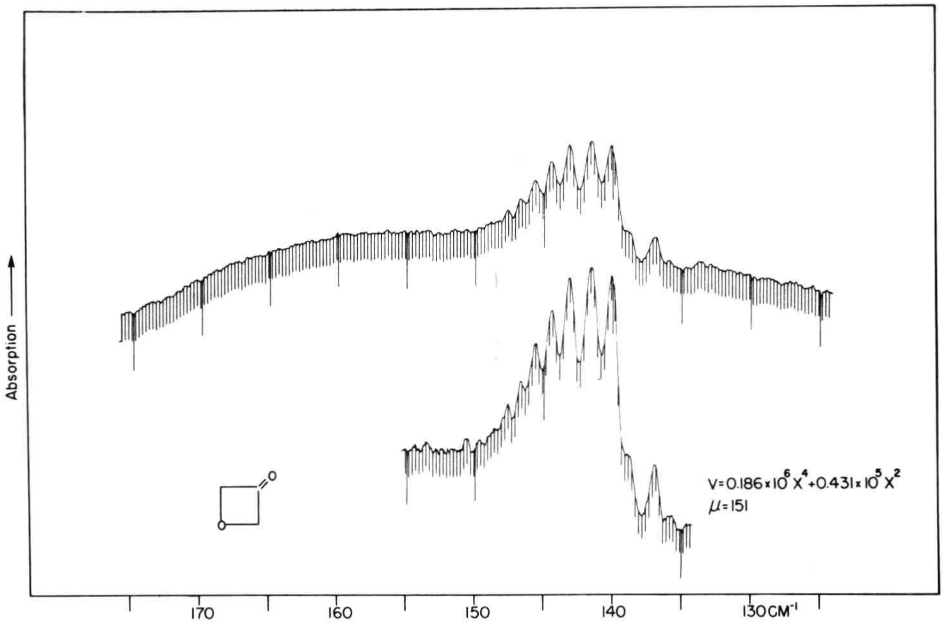

Fig. 2.1. Far infrared spectrum of oxetanone-3. The Q-branch transitions are shown on the background of overlapped P and R transitions. P = 22 torr, pathlength = 30 cm. Absorption is plotted upward in this spectrum.
[Reproduced from Carreira, L. A., Lord, R. C.: J. Chem. Phys. *51*, 3225 (1969).]

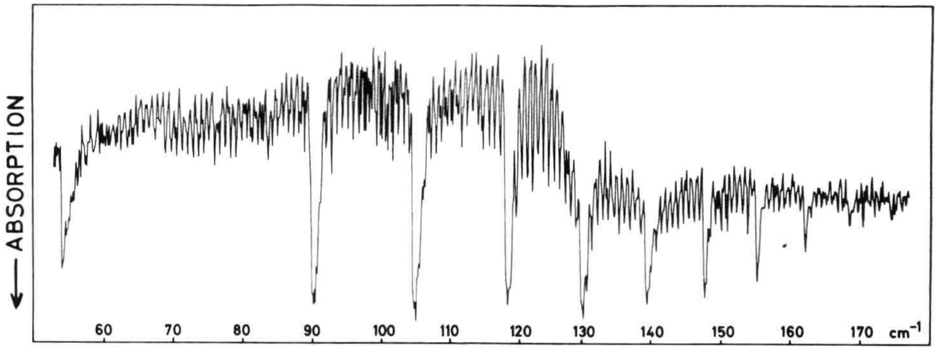

Fig. 2.2. Far infrared spectrum of oxetanone determined interferometrically. P = 48 torr, pathlength = 1 m. Absorption is plotted downward in this spectrum.
[Reproduced from Jokisaari, J., Kauppinen, J.: J. Chem. Phys. *59,* 2260 (1973)]

later in Fourier-transform interferometers$^{9)}$. Figure 2.1 shows the spectrum of oxetanone-3 recorded with a grating spectrometer$^{10)}$ and Fig. 2.2 depicts the spectrum of oxetane as computed from the scans of an interferometer$^{9)}$. Both these spectra represent great improvements over those obtained in earlier studies$^{5)}$ and the quantitative interpretation of the spectra is correspondingly improved. For the details of far-infrared instrumentation and techniques, the reader is referred to the monograph of Moeller and Rothschild$^{11)}$.

In the mid infrared region, ring-puckering vibrations may be seen as combination and difference bands with another normal mode of vibration, as was first shown by Ueda and Shimanouchi$^{12)}$. The combination and difference bands for cyclobutane between the ring-puckering mode and the B_2 deformation frequency near 1450 cm^{-1} are illustrated in Fig. 2.3, taken from Miller and Capwell$^{13)}$. All of the combination and difference transitions (except the first difference line) involve ring-puckering energy levels in both the excited state and the ground state of the mid infrared normal mode. Since the ring-puckering energy levels in the excited state of the mid infrared normal mode may be different from those in the ground state, appropriate differences between the combination bands and difference bands must be taken to

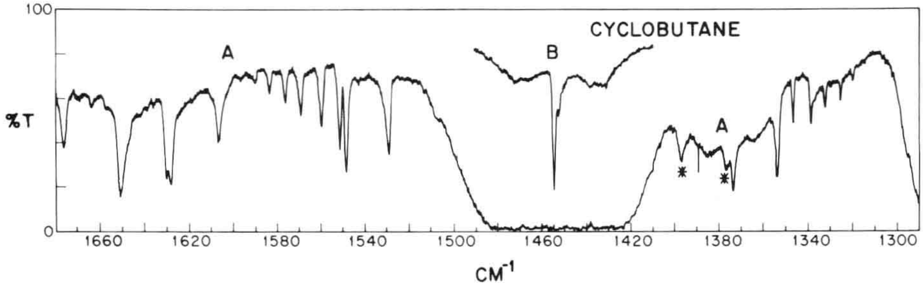

Fig. 2.3. Combination and difference band progressions involving the ring puckering vibration and a CH_2 scissoring mode in the mid-infrared spectrum of cyclobutane.
[Reproduced from Miller, F. A., Capwell, R. J.: Spectrochim. Acta *27A*, 947 (1971).]

obtain ring-puckering energy level differences between levels of the same parity in the ground state of the mid infrared mode. The symmetry of the mid infrared mode should be such that the combination and difference bands yield type-c band contours. For most C_{2v} molecules the B_2 ring-puckering mode will yield type-c sum and difference bands when the mid infrared reference band has symmetry A_1. The reference band is usually seen as a polarized fundamental in the Raman spectrum. Combination and difference bands with fundamentals of other symmetries are usually too weak or diffuse to be seen. Interpretation of the sum and difference bands can often be complicated by many other weak bands in the same region. For this reason the combination-difference band technique is usually used when no other technique is available to obtain the values of the ring puckering energy levels.

B. Raman Spectroscopy

With recent advances in laser technology, Raman spectroscopy has become a powerful tool for the direct observation of ring-puckering vibrational frequencies. Since the Raman signal in gases is extremely weak with respect to the exciting line, the use of high powered lasers, monochromators with low stray light, and efficient detection systems is necessary. The ring-puckering transitions with $\Delta v = 1$ are usually not totally symmetric and do not give rise to sharp Q branches in the Raman spectrum; on the contrary, the Raman lines of these non-totally symmetric vibrations tend to have broad contours with no discernible fine structure. However, the Raman spectra of small ring compounds show unexpected selection rules due to the very large amplitude of the

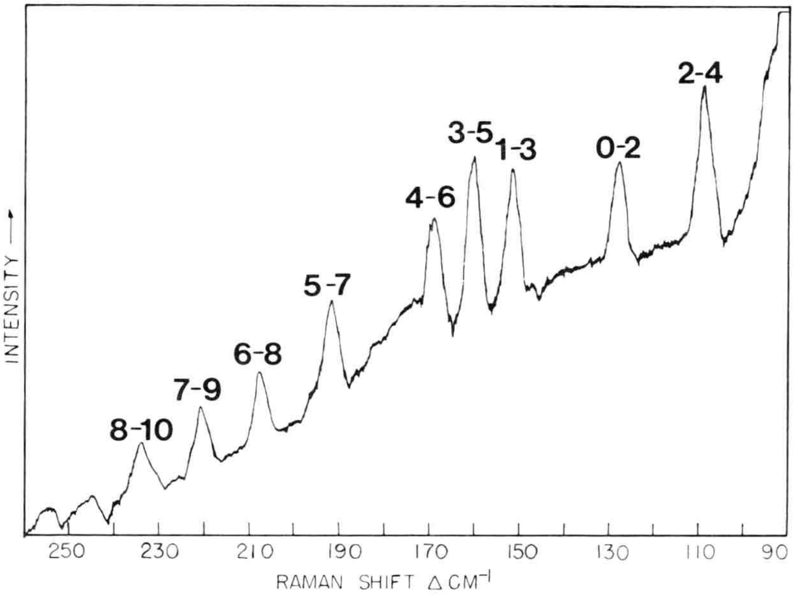

Fig. 2.4. Raman spectrum of cyclopentene.
[Reproduced from Chao, T. H., Laane, J.: Chem. Phys. Lett. *14,* 595 (1972).]

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ring-puckering vibrations. Both mechanical anharmonicity and electrical anharmonicity allow overtones of the ring-puckering vibration ($\Delta v = 2$) to be observed even when the transitions with $\Delta v = 1$ are too weak or diffuse to be observed. The overtone transitions are always totally symmetric (or have a totally symmetric component) and are Raman allowed. Since the isotropic polarizability terms are nonzero and usually larger than the anisotropic, a sharp Q branch structure will be observed for the overtones and this allows the individual hot bands to be assigned. The overtone vibrations are farther removed from the exciting line so that interference from the Rayleigh line and the pure rotational envelope is minimized.

Figure 2.4 shows the Raman spectrum of cyclopentene vapor$^{14)}$ in which all the Q branches correspond to transitions with $\Delta v = 2$. Many transitions with $\Delta v = 1$ fall in this same spectral range but are too weak or diffuse to be identified.

Since C-H stretching vibrations are very strong in the Raman spectra of compounds containing C-H groups, the combination-difference band technique for determining the ring-puckering energy levels may be of use when the laser power is not sufficient for direct observation of the overtone transitions. Here the direct product of the symmetry of the C-H fundamental and the ring-puckering fundamental must belong to the totally symmetric representation. For the most common C_{2v} case the symmetry of the ring-puckering vibration is B_2 and therefore the ring-puckering sum and difference bands will have sharp Q branches when the reference C-H stretching mode has symmetry B_2. The reference band will show a sharp Q branch in the infrared spectrum but will usually be very weak or missing in the Raman spectrum. The use of sum and difference combinations allows one to obtain ground state separations between the ring-puckering levels of the same parity$^{12, 13)}$.

C. Microwave Spectroscopy

The analysis of the microwave rotational spectra of small ring compounds can provide valuable information about the nature of large-amplitude ring-puckering potential functions. The type of information obtained may vary, depending on the potential function.

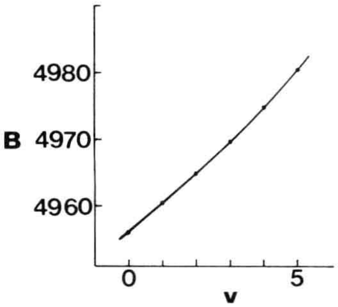

Fig. 2.5. Variation of the B rotational constant (in MHz) with ring-puckering vibrational state for oxetanone-3. Similar variations are found for the A and C rotational constants. [Reproduced from Gibson, J. S., Harris, D. O.: J. Chem. Phys. *57*, 2318 (1972).]

Due to the large amplitude of vibration, a significant contribution to the effective rotational constants may be made by the ring-puckering vibration. For the simplest case, that of a molecule with a single-minimum potential function, the rotational spectra for low J transitions may be fitted with a rigid-rotor Hamiltonian. Since the vibrational frequency is low, rotational transitions in a number of excited states of the ring-puckering vibration may be observed. As opposed to the linear dependence on vibrational state expected for a small amplitude vibration, the dependence for a large-amplitude mode may exhibit curvature. This is shown in Fig. 2.5 for oxetanone-3[15]. The curvature yields information on the aharmonicity of a single-minimum potential function.

The variation of rotational constants with ring-puckering vibrational state is very sensitive to the presence of a barrier at the planar conformation. This is shown for cyclobutanone[16] and methylenecyclobutane[17] in Fig. 2.6. The presence of a very small barrier, ca. 7.6 cm^{-1} in the case of cyclobutanone, causes deviation from a smooth variation for the lower levels. In the case of methylenecyclobutane, a very pronounced zig-zag of the rotational constants is observed due to the presence of a 140 cm^{-1} barrier. The dependence of the rotational constants on vibrational state may be used quantitatively to determine the shape of the potential function as discussed in subsequent sections.

In addition, for molecules with double-minimum potential functions where vibrational levels coalesce to form inversion doublets, the microwave data may yield very accurate values for these small vibrational spacings. The microwave rotational spectrum in these states may deviate significantly from that expected for a rigid-rotor model. Since the vibrational energy spacing for this pair of levels is no longer much greater than rotational energy spacings, it is not always possible to separate the vibrational and rotational Hamiltonians. An energy level diagram for the inversion doublet in trimethylene sulfide[18] is shown in Fig. 2.7. The vibrational spacing,

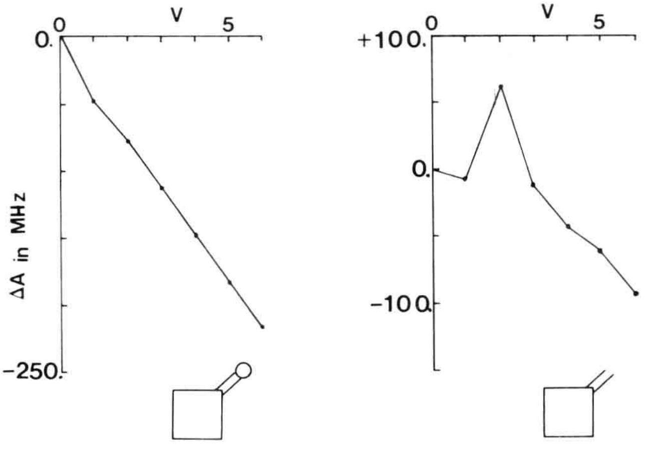

Fig. 2.6. Variation of the A rotational constants (in MHz) with ring-puckering vibrational state for cyclobutanone and methylene-cyclobutane.
[Reproduced from (A) Scharpen, L. H., Laurie, V. W.: J. Chem. Phys. *49*, 221 (1968); (B) J. Chem. Phys. *49*, 3041 (1968).]

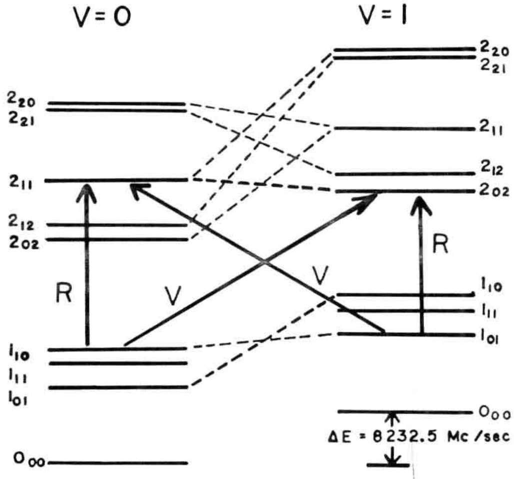

Fig. 2.7. Interactions between rotational levels in the v = 0 and v = 1 states of trimethylene sulfide.
[Reproduced from Harris, D. O., Harrington, H. W., Luntz, A. C., Gwinn, W. D.: J. Chem. Phys. *44*, 3467 (1966).]

8232.5 MHz (ca. 0.27 cm^{-1}) is quite small, in the microwave region. The interactions between rotational levels which are allowed by symmetry are shown by dashed lines.

A recent review of ring-puckering vibrations with emphasis on the theory and applications of microwave spectroscopy has appeared. The reader is referred to this work for further details$^{19)}$.

III Theoretical Basis for Interpretation of the Spectra

A. Introduction

In this section, we outline a procedure for obtaining a Hamiltonian for the treatment of low-frequency vibrations in molecules. We do this, in particular, to point out the justification for some of the Hamiltonians used in the past and to make clear the nature of the approximations involved in arriving at a specific Hamiltonian. Since there is danger of overinterpreting the results obtained from approximate Hamiltonians, we indicate some of the pitfalls in doing so.

The emphasis in this section is on the form of the kinetic energy operator. The choice of potential energy functions is considered in Section IV dealing with specific molecules. Emphasis is also placed on treatment of the vibrational data since a review emphasizing treatment of microwave data for ring puckering has appeared recently$^{19)}$.

We start by writing the classical kinetic energy expression for a non-linear molecule in a center-of-mass coordinate system. No distinction is made between small and large vibrational coordinates at this stage. We then rewrite the expression in a form suitable for obtaining the quantum mechanical kinetic energy operator. At that point, approximations are made to simplify the Hamiltonian and then we proceed to the treatment of the large-amplitude ring vibrations in molecules.

B. The General Hamiltonian

The kinetic energy for a molecule in a center-of-mass coordinate system may be written as

$$2T = (\boldsymbol{\omega}^t, \dot{\mathbf{q}}^t) \begin{pmatrix} \mathbf{I} & \mathbf{X} \\ \mathbf{X}^t & \mathbf{Y} \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega} \\ \dot{\mathbf{q}} \end{pmatrix} \tag{3.1}$$

where t denotes transpose. In this equation, for a nonlinear molecule of N atoms, $\boldsymbol{\omega}$ is a 3-dimensional column vector of the angular-velocity components of the molecule-fixed coordinate system relative to a system whose orientation is fixed in the laboratory. The time derivatives of the vibrational coordinates form the 3N-6 dimensional column vector $\dot{\mathbf{q}}$. **I** is the 3 x 3 dimensional instantaneous inertial tensor,

$$\mathbf{I} = \begin{pmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{yx} & I_{yy} & -I_{yz} \\ -I_{zx} & -I_{zy} & I_{zz} \end{pmatrix} \tag{3.2}$$

$$I_{kk} = \sum_{\alpha=1}^{N} m_\alpha (\mathbf{r}_\alpha \cdot \mathbf{r}_\alpha - r_{\alpha k}^2); \quad k = x, y \text{ or } z \tag{3.3a}$$

$$I_{kk'} = \sum_{\alpha=1}^{N} m_\alpha r_{\alpha k} r_{\alpha k'}; \quad k \neq k' \tag{3.3b}$$

where

m_α = mass of the α'th atom
$\mathbf{r}_\alpha$ is the coordinate vector of the α'th atom in the center-of-mass system
$r_{\alpha k}$ denotes the k'th component of the α'th vector.

Y in Eq. (3.1) is (3N-6) x (3N-6) with elements defined by

$$Y_{ij} = \sum_{\alpha=1}^{N} m_\alpha \left(\frac{\partial \mathbf{r}_\alpha}{\partial q_i}\right) \cdot \left(\frac{\partial \mathbf{r}_\alpha}{\partial q_j}\right) \tag{3.4}$$

X is 3 x (3N-6) with elements defined by

$$X_{ki} = \sum_{\alpha=1}^{N} m_\alpha \left[\mathbf{r}_\alpha \times \left(\frac{\partial \mathbf{r}_\alpha}{\partial q_i}\right)\right]_k \tag{3.5}$$

where k denotes the k'th component of the cross product. Expanding Eq. (3.1) we obtain

$$2T = \sum_{k} I_{kk}\omega_k^2 - \sum_{k,k'} I_{kk'}\omega_k\omega_{k'} + \sum_{i}\sum_{j} Y_{ij}\dot{q}_i\dot{q}_j + 2\sum_{k}\sum_{i} X_{ik}\omega_k\,\dot{q}_i \qquad (3.6)$$

where k,k' = x, y, or z; and i, j run over the vibrational coordinates.

The first two terms are pure rotational terms, the third a pure vibrational term, and the last a Coriolis term. The partitioning of the energy between the pure rotational terms and the Coriolis term depends on the choice of the rotating axis system used to describe the problem$^{18-22)}$.

In order to obtain a quantum mechanical kinetic energy operator, a momentum representation of the kinetic energy is required. If coordinates are chosen having conjugate momenta

$$\mathbf{P} = \left(\frac{\partial T}{\partial \boldsymbol{\omega}}\right) \qquad (3.7)$$

and

$$\mathrm{p} = \left(\frac{\partial T}{\partial \dot{q}}\right) \qquad (3.8)$$

where **P** is a 3-dimensional vector of angular momentum components and **p** is a 3N-6-dimensional vector of the momenta conjugate to q, the momentum representation of the kinetic energy is obtained simply by inverting the 3 N-3 x 3 N-3 matrix appearing in Eq. (3.1):

$$2T = (\mathbf{P}^t, \mathbf{p}^t)\begin{pmatrix}\mathbf{I} & \mathbf{X}\\ \mathbf{X}^t & \mathbf{Y}\end{pmatrix}^{-1}\begin{pmatrix}\mathbf{P}\\ \mathbf{p}\end{pmatrix} \qquad (3.9)$$

The 3 N-3 x 3 N-3 matrix in Eq. (3.9) is hereafter referred to as the rotation-vibration **G** matrix. Transformation to the correct quantum mechanical from according to Kemble$^{23)}$ yields

$$\begin{aligned}2T &= g^{1/4}\sum_{k}\sum_{k'} P_k g^{-1/2} g_{kk'} P_{k'} g^{1/4}\\ &+ g^{1/4}\sum_{i}\sum_{j} p_i g^{-1/2} g_{ij} p_j g^{1/4} \qquad (3.10)\\ &+ g^{1/4}\sum_{k}\sum_{i}\left(P_k g^{-1/2} g_{ki} p_i + p_i g^{-1/2} g_{ik} P_k\right) g^{1/4}\end{aligned}$$

where $k,k' = x, y$ or z and i, j run over the vibrational coordinates. In this equation, g_{mn} denotes the appropriate element of the rotation-vibration **G** matrix [Eq. (3.9)] and g is the value of its determinant. The P_k are the components of the quantum mechanical angular momenta and the p_i the vibrational momentum operators $\frac{\hbar}{i}\frac{\partial}{\partial q_i}$. In general, g and the g_{mn} may be functions of the coordinates and thus may not commute with the momenta. The three terms are identified, as before [Eq. (3.6)], as the kinetic energy of pure rotation, pure vibration and vibration-rotation interaction, respectively.

In principle, it is possible to choose a rotating axis system and evaluate numerically the coordinates and coordinate derivatives required to compute the elements of **I**, **X** and **Y** [Eq. (3.1)] for a given dynamical model. By doing this for a grid of values of the 3N-6 vibrational coordinates and obtaining the vibration-rotation **G** matrix by inversion of the $\mathbf{G}^{-1}$ matrix at each grid point, we may obtain a rather complete description of the vibration-rotation kinetic energy [Eq. (3.9)]. By expressing the g_{mn}, $g^{1/4}$ and $g^{-1/2}$ in multidimensional Taylor series or mixed Taylor-Fourier series, an accurate quantum mechanical kinetic energy operator could be written for the dynamical model used and for the particular choice of rotating axes. As pointed out by Gwinn and Gaylord¹⁹⁾, the solutions of the eigenvalue problems associated with a vibration-rotation problem do not and *must not* depend on the choice of the rotating axis system as long as an adequate Hamiltonian is used. What do depend on the axis system used are the numerical values of elements of the inertial tensor or vibration-rotation interaction constants determined from analysing the data.

For all but the smallest molecules, the procedure outlined in the previous paragraph is impractical. If we can locate or approximate the vibrational band origins from the experimental data, simplifications result. We then treat the J = 0 states in which case all terms in Eq. (3.1) involving rotational angular momenta vanish. Rewriting the pure vibrational term we obtain the vibrational kinetic energy T_v:

$$2T_v = \sum_i \sum_j p_i g_{ij} p_j + 2V'(q) \tag{3.11}$$

The term $V'(q)$ has been referred to as a "pseudopotential" term because it lends itself to expansion in a Taylor (or Fourier) series in the vibrational coordinates and may be absorbed into the effective potential. $V'(q)$ is given by

$$\begin{aligned} V'(q) &= \frac{\hbar^2}{8} \sum_i \sum_j \left(\frac{\partial}{\partial q_i}\, g_{ij} \left(\frac{\partial \ln g}{\partial q_j}\right)\right) \\ &+ \frac{\hbar^2}{16} \sum_i \sum_j \left(g_{ij} \left(\frac{\partial \ln g}{\partial q_i}\right)\left(\frac{\partial \ln g}{\partial q_j}\right)\right) \end{aligned} \tag{3.12}$$

The total vibrational Hamiltonian is then given by

$$H_v = -\frac{\hbar^2}{2} \sum_i \sum_j \frac{\partial}{\partial q_i}\, g_{ij} \frac{\partial}{\partial q_j} + V'(q) + V(q) \tag{3.13}$$

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