

Unimolecular Reaction Dynamics

Theory and Experiments

TOMAS BAER
AND
WILLIAM L. HASE

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UNIMOLECULAR REACTION DYNAMICS

Theory and Experiments

Tomas Baer
and
William L. Hase

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Preface and Acknowledgments

The field of unimolecular reactions has been revolutionized during the past 20 years by a series of new developments in both experimental techniques and theoretical advances. The precise information about the dissociation of large and small molecules and ions that is now being routinely collected has permitted the testing of the most detailed aspects of the theory. These advances have come about through a wonderful interplay between experimentalists and theoreticians. We hope that this book transmits not only information, but also the excitement in the field that has kept so many of us absorbed.

In many ways, this book is a community effort. The field of unimolecular reactions has progressed to this point through the combined efforts of many scientists located in all parts of the globe. In the early stages of this work, we received numerous and excellent suggestions about the contents and structure of the book. Finally, many individuals read sections of the manuscript while we were preparing them. Among these people are Elliot Bernstein, Terry Gough, Stephen Gray, William Green, Paul Houston, Steve Klippenstein, Cornelius Klots, Kevin Lehmann, Chava Lifshitz, Robert Marquardt, Roger Miller, Will Polik, Hanna Reissler, Ned Sibert, Kihyung Song, and Howard Taylor. Special thanks go to some who have made major contributions to this book; among these are Jon Booze, Martin Hunter, Gilles Peslherbe, and Ling Zhu, whose insightful comments and suggestions have profoundly influenced the content of chapters 7 and 9. As with any work of this sort which attempts to review a large field of research, we have attempted to refer to as many studies as seems reasonable. However, we are fully aware that much excellent work has not been cited. To the extent possible, we have referred to studies which have been addressed by both experiment and theory.

TB is grateful to the UNC departments of chemistry and romance languages, which permitted him to spend all of 1992 with the UNC Year in Montpellier, France exchange program where the first drafts of several chapters were written. Reading and digesting the many excellent papers between croissant breakfasts and beers at sidewalk cafes is a memory not readily forgotten. This volume was written by the authors working in separate locations, a mode made possible by the marvels of electronic mail and FAX. However, a week spent together in the Virginia mountains was an essential and memorable element for progressing past various bottlenecks and completing the manuscript.

WLH wishes to acknowledge the inspiration provided by his research advisors John W. Simons and Don L. Bunker, who acquainted him with unimolecular reactions and pointed out the beautiful detail and nuances of their dynamics. We both acknowledge our debt to the many graduate students and postdocs who have passed through our laboratories. The stimulation provided by students is something that all of us in the academic life share and treasure. The writing of this book has been a major preoccupa-

tion for us during the past three years. We are especially grateful to Carol and Cris for their generous understanding, their encouragement, and above all their faith that we would some day finish this book.

Chapel Hill, NC
August 1995

T.B.

Detroit, MI
August 1995

W.L.H.

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Unimolecular Reaction Dynamics

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Introduction

The field of unimolecular reactions has witnessed impressive advances in both experimental and theoretical techniques during the past 20 years. These developments have resulted in experimental measurements that finally permit critical tests of the major assumptions made more than 60 years ago when Rice and Ramsperger (1927, 1928) and Kassel (1928) first proposed their statistical RRK theory of unimolecular decay. At the heart of these advances is our ability to prepare molecules in narrow ranges of internal energy, even in single quantum states, at energies below and above the dissociation limit. This has led to detailed spectroscopic studies of intramolecular vibrational energy redistribution (IVR), a process that is intimately related to the assumption of random energy flow in the statistical theory of unimolecular decay.

This book is devoted exclusively to the study of state- or energy-selected systems. However, in order to place these studies in the context of the much larger field of unimolecular reactions in general, we provide a brief background of the field up to about 1970. The experimental studies of unimolecular reactions developed in three stages. The early studies involved strictly thermal systems in which molecules were energized by heating the sample either in a bulb (Chambers and Kistiakowsky, 1934; Schlag and Rabinovitch, 1960; Flowers and Frey, 1962; Schneider and Rabinovitch, 1962), or by more sophisticated methods such as shock tubes which were applied to unimolecular reactions by Tsang (1965, 1972, 1978, 1981) and others (Astholz et al., 1979; Brouwer et al., 1983). The drawback of these studies is that molecules were prepared in a very broad (albeit well characterized) distribution of internal energy states. A major advance was the use of chemical activation in the early 1960s in which a species such as CH_2 reacted with a molecule, thereby forming an energized species which could either isomerize or be stabilized by collisions (Rabinovitch and Flowers, 1964; Rabinovitch and Setser, 1964; Kirk et al., 1968; Hassler and Setser, 1966; Simons and Taylor, 1969). This approach permitted the reacting species to be prepared in a narrow range of internal energies. However, the number of reactions that could be investigated was small, the energy selection was not very precise, and the range of internal energies was very limited. In addition, in both the thermal and chemical activation studies, the time base for measuring the dissociation rate was the rather imprecise collisional relaxation rate. Many of the early studies dealing with thermal systems and chemical activation have been the subject of two excellent books on unimolecular reactions (Forst, 1973; Robinson and Holbrook, 1972). More recently a book which focuses primarily on thermal unimolecular and the related three-body recombination reactions, as well as collisional energy transfer processes, has appeared (Gilbert and Smith, 1990).

The third stage in the study of unimolecular reactions (the subject of this book) began in the early 1970s with the development of more general and precise methods of

energy and state preparation as well as the development of absolute time bases for measuring reaction rates. Molecules and ions can be prepared above their dissociation limits by laser excitation with wavenumber resolution. With the use of two or more pulsed lasers, the reaction can be monitored as a function of time from milliseconds to femtoseconds. Less dramatic advances in photoelectron photoion coincidence (PEPICO) allow ionic dissociation rates to be studied with an energy resolution of about 100 cm^{-1} over a time range from 10^{-4} to 10^{-7} sec.

Our theoretical understanding of unimolecular reactions has kept pace with the advances in experimental techniques. As a result of powerful computers, the geometry of the reacting molecule as well as its vibrational frequencies can now be calculated as a function of the reaction coordinate from the beginning to the end of the reaction. The results of these calculations provide sufficient information to treat the reaction with much greater sophistication than was previously possible. In addition, accurate potential energy surfaces have permitted reactions to be investigated by classical trajectory and quantum dynamics methods, approaches that are not inherently limited by the assumptions of the statistical theory.

1.1 WHAT IS A UNIMOLECULAR REACTION?

A unimolecular reaction is defined as any system that evolves in time as a result of some prior stimulus or excitation step. Thus, both dissociation and isomerization are examples of unimolecular processes. Phenomenologically, a unimolecular reaction, $A \rightarrow \text{products}$, is written as

$$-\frac{d[A]}{dt} = k[A], \quad (1.1)$$

which, when integrated, gives rise to the time dependence of the concentration of $A(t)$:

$$[A] = [A_0]e^{-kt}, \quad (1.2)$$

where k is the unimolecular rate constant with units of reciprocal time, and $[A_0]$ is the concentration of species A at time, $t = 0$. The rate constant k depends on the internal energy of A , or in the case of an equilibrium ensemble of A , its temperature. For a given state of excitation, the exponential decay is a result of the assumption that the rate is a function only of the concentration of A .

The important questions in the study of unimolecular reactions are (a) what is the initial state produced in the excitation step, (b) how fast does the system evolve toward products, (c) what are the reaction products, and (d) what are the product energy states? Up until about 1975, the first and last questions could not be addressed experimentally. Most experiments were carried out with the reacting system specified in terms of a temperature with its attendant distribution of initial states. From the very beginning, it was recognized that a dissociation rate depends on the internal energy of the molecule (Hinshelwood, 1926). Thus, all detailed statistical theories of unimolecular reactions begin with the calculation of $k(E)$, the rate constant as a function of the internal energy, E .

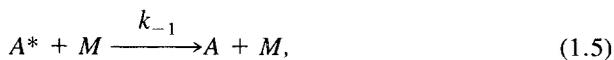
The connection between $k(T)$, often called the canonical rate constant, and $k(E)$, the microcanonical rate constant, involves averaging $k(E)$ over the energy distribution

$$k(T) = \int_{E_0}^{\infty} P(E,T)k(E)dE, \quad (1.3)$$

where E_0 is the activation energy and $P(E,T)$ is the distribution of internal energies at a given temperature, T . In many applications the quantity of interest is $k(T)$ because most natural systems can be described adequately by a thermal distribution characterized by a given temperature. However, there are many important exceptions such as flames, discharges, and explosions. For such systems it is important to know $k(E)$ as well as $P(E,T)$. Perhaps a more important reason for studying $k(E)$ rather than $k(T)$ is that the theory can be tested adequately only by comparing the measured and calculated $k(E)$. Once this has been accomplished, the rate constant of any system with a known distribution of internal states can be calculated.

1.2 THERMALLY ACTIVATED EXPERIMENTS AND THE LINDEMANN MECHANISM

Our basic understanding of unimolecular reactions can be traced to Lindemann (1922), who proposed that reacting molecules in a thermal system are energized by collisions and that the mechanism for the reaction can be expressed as



where A^* represents a molecule that is sufficiently excited to react with no further input of energy. M is any molecule in the vessel. Assuming a steady-state production of A^* , we can readily show that the overall rate of product formation is given by

$$\text{Rate} = k_2[A^*] = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} = k_{\text{uni}}[A] \quad (1.7)$$

The interesting feature of this rate law is that the phenomenological unimolecular rate constant, k_{uni} , changes from second order (in A and M) at low pressures where $k_{-1}[M] \ll k_2$, to first order in $[A]$ at high pressures. The high-pressure rate constant is then simply $k_{\infty} = k_1 k_2 / k_{-1}$. When data are plotted as $k_{\text{uni}}/k_{\infty}$ versus the pressure $[M]$, the famous “fall-off” plots are obtained. An example of such a plot is shown in figure 1.1 for the case of cyclopropane isomerization (Prichard et al., 1953). The change from second order (the straight-line portion at low pressures) to unimolecular (independent of the pressure) is shown very convincingly in these results. This reaction, and variations thereof, were studied more than any other during the 1950s and 1960s (Butler and Kistiakowsky, 1960; Slater, 1953; Prichard et al., 1953; Schlag and Rabinovitch, 1960).

According to Eq. (1.7), the fall-off plot depends not only on the value of the unimolecular rate constant, k_2 , but also on the collisional activation, k_1 , and deactivation, k_{-1} , rate constants. The bimolecular reactions both complicate and aid the analysis of the rate data. On the one hand, three rate constants must be determined. On the other hand, with appropriate assumptions, the bimolecular collisions serve as a time

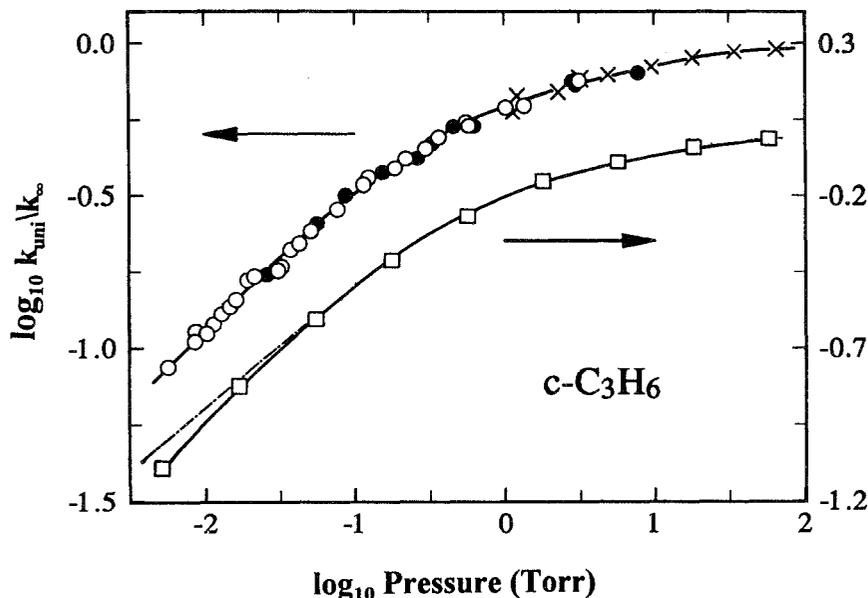


Figure 1.1 Pressure dependence of the unimolecular rate constant for $c\text{-C}_3\text{H}_6 \rightarrow \text{H}_2=\text{CH}-\text{CH}_3$. The open and closed circles are data from Prichard et al. (1953) while the x's are data of Chambers and Kistiakowsky (1934). The lower curves are displaced down by 0.3 log units. The solid lines are the experimental results, the open squares are calculated by Slater (1953) assuming 13 active oscillators (in place of the full 21), and the dashed curve is a Kassel or RRK calculation with 13 oscillators by Prichard et al. (1953). Taken in modified form, and with permission, from Prichard et al. (1953).

base so that k_2 can be determined relative to the collision frequency. However, to do so requires assumptions about the collisional deactivation efficiency, $k_{-1}[M]$. The crudest assumption is the strong-collision assumption in which it is supposed that a single collision will deactivate A^* . With this assumption, $k_{-1}[M]$ is just given by the collision frequency, ω . In light of recent collisional energy transfer studies (Gilbert et al., 1983; Hippler et al., 1981, 1983; Jalenak et al., 1988; Weston and Flynn, 1992; Gilbert and Smith, 1990), the deactivation step can now be treated with considerably greater sophistication.

At this point it is useful to consider again Eq. (1.2), which states that the time evolution of an ensemble of molecules is given by an exponential function. This has been amply verified by numerous experiments in thermal systems. Yet we note that a canonical distribution, which contains molecules in a large distribution of internal energies, is not characterized by a single rate constant and therefore cannot evolve by a single exponential decay. Rather, the time behavior of such a system should be described by a weighted sum of exponential decays given by

$$[A(t)] = [A_0] \int P(E, T) k(E) e^{-k(E)t} dE. \quad (1.8)$$

The explanation for this paradox is that a canonical or thermal system maintains the equilibrium distribution of internal energy states through collisions. Thus, Eq. (1.8) does not describe the time behavior of a canonical ensemble. What it does describe is a

hypothetical system in which thermal equilibrium has been established at some time, but which from then on evolves with no collisions. In such a system, the energy-rich molecules will decay first with short lifetimes, while the lower-energy molecules decay with longer lifetimes.

1.3 THE RRK AND RRKM/QET THEORIES

The Lindemann mechanism consists of three reaction steps. Reactions (1.4) and (1.5) are bimolecular reactions so that the true unimolecular step is reaction (1.6). Because the system described by Eqs. (1.4)–(1.6) is at some equilibrium temperature, the high-pressure unimolecular rate constant is the canonical $k(T)$. This can be derived by transition state theory in terms of partition functions. However, in order to illustrate the connection between microcanonical and canonical systems, we consider here the case of $k(E)$ and use Eq.(1.3) to convert to $k(T)$.

The conceptual framework for understanding the unimolecular reaction (1.6) was developed by Rice and Ramsperger (1927, 1928) and Kassel (1928). The dissociating system is treated as an assembly of s identical harmonic oscillators, one of which is truncated at an energy E_o , the activation energy for dissociation. If the dissociative, or critical oscillator happens to have an energy, ϵ , in excess of the activation energy, the molecule dissociates. A fundamental assumption of the theory is that energy flows statistically among all of the oscillators and that the chance of finding the system with a particular arrangement of its internal energy is equivalent to any other. The dissociation rate is then proportional to the probability that for a given total energy, $E = nh\nu$, the critical oscillator contains an energy equal to, or greater than $E_o = mh\nu$. The problem reduces to a combinatorial determination of fitting n quanta into the various oscillators. The number of ways of distributing n quanta (the total energy) among the s oscillators is $(n + s - 1)!/n!(s - 1)!$. This is the degeneracy of a state with n quanta of s equally spaced oscillators. The number of ways that the n quanta can be placed in the molecule such that at least m quanta are in the critical oscillator is given by $(n - m + s - 1)!/(n - m)!(s - 1)!$. The probability of the molecule being in a dissociative state is then just the ratio of these probabilities, or

$$\text{Probability} = \frac{(n - m + s - 1)! n!}{(n - m)!(n + s - 1)!} \quad (1.9)$$

This quantum expression can be simplified by assuming that the spacing is very small so that n and m are very large. With this assumption we can apply Sterling's approximation for the factorial functions, which is $h! = h^h/e^h$. If in addition the number of quanta is much larger than the number of oscillators, that is $(n - m) \gg s$, then $(n - m + s - 1)$ can be replaced by $(n - m)$ (but not in the exponent!). The probability then reduces to

$$\text{Probability} = \left(\frac{n - m}{n} \right)^{s-1} \quad (1.10)$$

This expression is converted to a rate constant by multiplying the probability by a rate of passage to products. In the spirit of this model, the rate is just the vibrational frequency ν . Thus the unimolecular rate constant is given by

$$k(E) = \nu \left(\frac{n-m}{n} \right)^{s-1} = \nu \left(\frac{E-E_0}{E} \right)^{s-1} \quad (1.11)$$

The expression in terms of the energies are obtained by multiplying top and bottom by $(h\nu)^{s-1}$.

This RRK expression for the rate contains two important features. First, it predicts that the rates are a strong function of the number of vibrational oscillators s . Second, it predicts that the rate increases rapidly with excess energy, $(E - E_0)$. Although both of these conclusions are correct, Eq. (1.11) unfortunately is incapable of giving the correct rate, even within an order of magnitude. There are several reasons. First, the assumption of classical oscillators with $(n - m) \gg s$ is inappropriate for most chemical systems. For instance, a molecule such as benzene, with its 12 atoms, has $s = 30$. At an energy of 20,000 cm^{-1} above the dissociation limit, $n - m \approx 20$ (assuming an average vibrational frequency of 1000 cm^{-1}). In most chemically interesting situations, $s \approx n - m$. This has forced workers to use s values that are artificially lower than the number of oscillators. Reasonable agreement with experiment is generally obtained when s is equal to about one half of the total oscillators [see fig. 1.1 and also Weston (1986)]. A second shortcoming of the classical RRK theory is the neglect of the zero point energy. However, the theory can be fixed up to account for the zero point energy, a process that led Whitten and Rabinovitch (1963, 1964) to propose a very useful and interesting method for determining accurate densities of states.

The problems associated with the classical RRK expression in Eq. (1.11) were eliminated by Marcus and Rice (1951) and by Rosenstock, Wallenstein, Wahrhaftig, and Eyring (1952). These quantum theories, which treat the vibrational (and rotational) degrees of freedom in detail, became known as the RRKM and the quasi-equilibrium theory (QET), respectively. The RRKM/QET expression, which will be discussed in detail in chapter 6, is given by

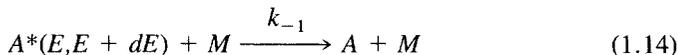
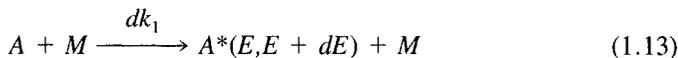
$$k(E) = \frac{\sigma N^\ddagger(E - E_0)}{h\rho(E)}, \quad (1.12)$$

where $\rho(E)$ is the density of vibrational states at the energy E , $N^\ddagger(E - E_0)$ is the sum of the vibrational states from 0 to $E - E_0$ in the transition state, h is Planck's constant, and σ is the reaction symmetry factor. For simplicity, the role of rotations is not included in Eq. (1.12). A major difference between RRKM and RRK theory is that the former depends strongly on the values of the vibrational frequencies, while the latter does not. It is this RRKM/QET formulation which is the starting point for modern statistical theories.

For a decade, a rival theory due to Slater (1955, 1959) provided considerable motivation for more detailed experimental as well as theoretical investigations. This very interesting and elegant theory, which is discussed in more detail by Robinson and Holbrook (1972) and Nikitin (1974), as well as in chapter 8, is more akin to a dynamical than a statistical theory. Because the Slater theory treats the vibrations classically, it also requires the use of fewer oscillators to fit the experiment (see fig. 1.1). Its flawed fundamental hypothesis that the molecule's modes were strictly harmonic, thereby preventing energy flow among them, and its failure to account quantitatively for the experimentally measured rates led to its being quickly overshadowed by the successes of the RRKM/QET theory.

1.4. RRKM THEORY IN THE FALL-OFF REGION

Until about 1960, fall-off plots were the major source of quantitative information about unimolecular reactions. In order to adapt the microcanonical RRKM theory to these thermal data, it was necessary to take into account the internal energy of the reactants by rewriting Eqs. (1.4)–(1.6) as follows:



In this mechanism, dk_1 is the differential rate constant for producing the excited molecule in a range of energies from E to $E + dE$, and the energy dependence on the unimolecular decay is explicitly stated in $k(E)$. Imposing steady state on A^* leads to

$$dk_{\text{uni}} = \frac{dk_1 k(E)[M]}{k_{-1}[M] + k(E)} = \frac{k(E)(dk_1/k_{-1})}{1 + k(E)/(k_{-1}[M])}. \quad (1.16)$$

The total thermal unimolecular rate constant is obtained by integrating Eq. (1.16) over the energy range from E_0 to ∞ . As pointed out by Steinfeld et al. (1989), dk_1/k_{-1} is the equilibrium probability that the reactant molecule A^* has an energy in the range from E to $E + dE$. Thus, $dk_1/k_{-1} = P(E, T)dE$, where $P(E, T)$ is the thermal energy distribution of the molecule. The total unimolecular rate constant thus becomes

$$k_{\text{uni}}(T) = \int_{E_0}^{\infty} \frac{k(E)P(E, T)dE}{1 + k(E)/\omega}, \quad (1.17)$$

where ω is the collision frequency, $k_{-1}[M]$. This assumes that each collision between an excited A^* and a bath molecule results in a deactivation, in other words, the strong collision assumption.

Equation (1.17) can be evaluated using either the RRK or RRKM theory expressions. Proceeding with the latter, we note that

$$P(E, T) = \frac{\rho(E)e^{-E/k_B T}}{\int_0^{\infty} \rho(E)e^{-E/k_B T} dE} = \frac{1}{Q(T)} \rho(E)e^{-E/k_B T}, \quad (1.18)$$

where $Q(T)$ is the vibrational partition function. When the RRKM expression in Eq. (1.12) is substituted for $k(E)$ and Eq. (1.18) is used for $P(E, T)$, the unimolecular rate constant in Eq. (1.17) becomes

$$k_{\text{uni}}(T) = \frac{\sigma}{hQ(T)} \int_{E_0}^{\infty} \frac{N^\ddagger(E - E_0)e^{-E/k_B T}}{1 + k(E)/\omega} dE \quad (1.19)$$

For simplicity, the role of the rotations is ignored in Eq. (1.19). A similar expression is derived by Steinfeld et al. (1989) which includes the rotational energy explicitly.

The total unimolecular decay rate constant depends upon the gas pressure through the collision frequency ω . At high pressures, where it is independent of ω , it becomes

the canonical transition state theory rate constant (see chapter 6). However, in the interesting fall-off region Eq. (1.19) must be evaluated numerically. Equation (1.19) is capable of fitting experimental fall-off curves with the use of reasonable frequencies for the molecule and the transition state. An example for the $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ isomerization reaction is shown in figure 1.2 (Schneider and Rabinovitch 1962). Experiments of this type, carried out with various isotopic substituents, provided excellent agreement between theory and experiments without an arbitrary reduction in the

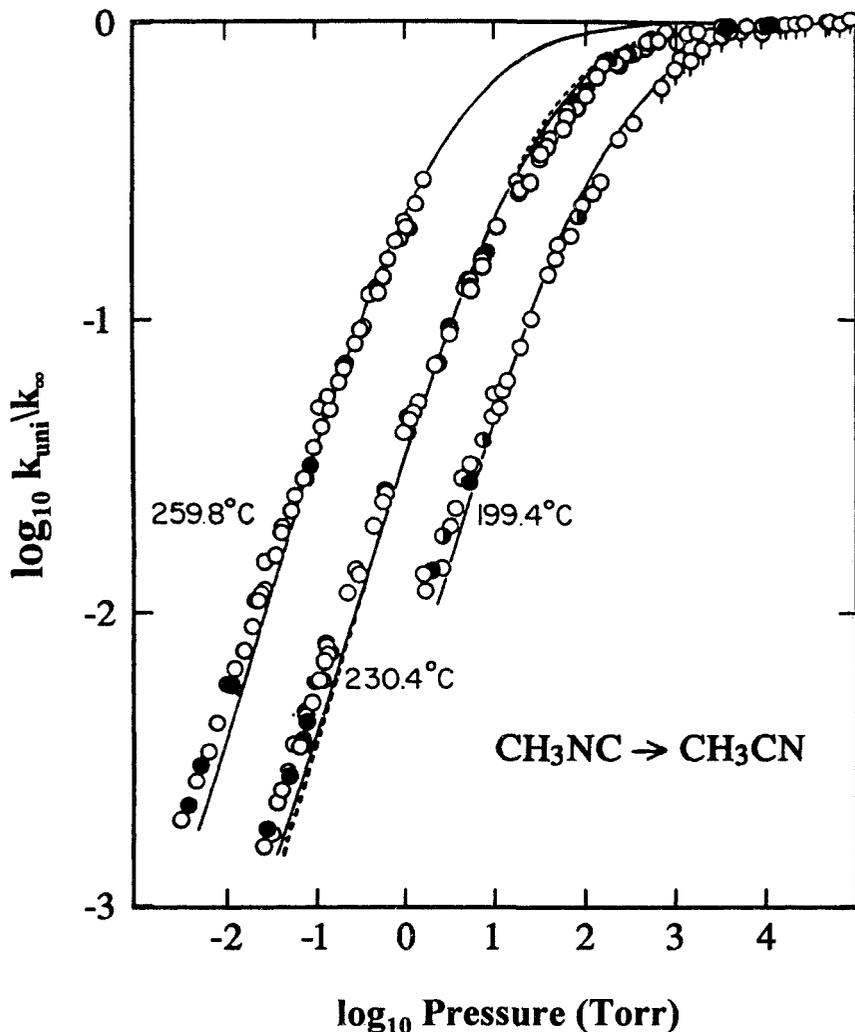


Figure 1.2 Pressure dependence of the unimolecular rate constant for $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ isomerization. For clarity, the 260° and 200° curves are displaced by one log unit to the left and right, respectively. (All three curves are nearly identical.) The solid lines through the data are RRKM calculated rates with the strong collision assumption. Taken with permission from Schneider and Rabinovitch (1962).

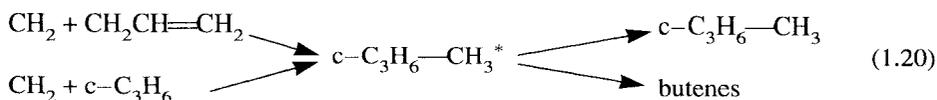
number of oscillators. However, the thermal nature of the experiments as well as the required integration over the energies reduced considerably the precision with which the theory could be tested.

1.5 CHEMICAL ACTIVATION EXPERIMENTS: A FIRST ATTEMPT AT $k(E)$

One of the major problems in the interpretation of the thermal data was that instead of depending on one rate constant, the overall rate was a function of three constants, none of which was easy to calculate. As a result, much effort was placed on developing simple models for the activation and deactivation steps so that interesting information about the unimolecular rate constant, $k(E)$ could be extracted. One of the big questions for many years was the number of collisions required to deexcite the activated molecule, A^* . According to the strong-collision model, a single collision sufficed, while other models attempted to treat the problem more delicately, but with no significantly greater success. Although the distinction between A and A^* is reasonably evident from the point of view of reactions 1.13–1.15, it is very crude when dealing with activation and deactivation steps. Thus, it was recognized that a different means for activating molecules must be found in order to isolate the unimolecular rate constant, $k(E)$.

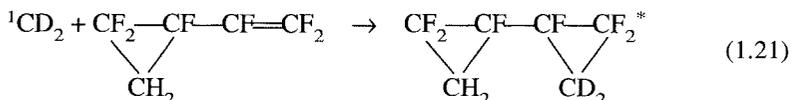
A successful approach to energy selection was achieved by a variety of groups using chemical activation (Butler and Kistiakowsky, 1960; Rabinovitch and Flowers, 1964; Rabinovitch and Setser, 1964; Kirk et al., 1968; Hassler and Setser, 1966; Rabinovitch et al., 1963; Simons and Taylor, 1969). In these experiments such high energy species as H, CH_2 , or C_2H_5 radicals were added to molecules, thereby producing an activated molecule with a somewhat well defined energy content. In one of the more famous experiments, a methylene group (CH_2) was added to ethylene, thereby forming an excited cyclopropane molecule. The internal energy is sufficient to cause the molecule to isomerize to propene. However, collisional deactivation could also stabilize the hot cyclopropane. This experiment not only removed the excitation step k_1 , it also replaced $k(T)$ by $k(E)$. By using methylene from the photolysis of either ketene or diazomethane, it was possible to adjust somewhat the internal energy of the CH_2 and thereby the total energy in the nascent cyclopropane. However, uncertainties in the state (singlet or triplet) of the CH_2 prevented clear interpretations of these energy-dependent studies. The more interesting parameter was the inert gas pressure. By adjusting the pressure, it was possible to vary the ratio of stabilized to isomerized product. The rate of stabilization increased with the pressure while the isomerization reaction (being unimolecular) was independent of the pressure. In this fashion, it was determined that A^* decays exponentially in time.

One of the major assumptions in the statistical theory of unimolecular decay is that energy flows or equilibrates rapidly among all of the oscillators prior to dissociation or isomerization. Several chemical activation experiments addressed this question directly and the results mostly confirmed the hypothesis. In one such study, Butler and Kistiakowsky (1960) chemically activated methylcyclopropane in two different ways:



In the first reaction, the methylene is added across a double bond, while in the second reaction, it is inserted in the C—H single bond. The other difference in the two methods for preparing the excited methylcyclopropane molecule is in the total energy. The heat of formation of propene is 8 kcal/mol less than that of cyclopropane so that second preparation of $C_4H_8^*$ gives an excited species with 8 kcal/mol more excitation. However, in view of the total energy deposited, this small difference was deemed unimportant. Initially, the energy is certainly deposited in different parts of the molecule. Yet, the fraction of butenes to methylcyclopropane was nearly the same at all pressures investigated. From the upper limit of the experiment, it was concluded that the energy is distributed randomly in less than 10^{-11} sec. Numerous such experiments lead to similar conclusions. In a limited number of cases, it was possible to vary the molecule's internal energy by preparing $C_2H_5F^*$ with a variety of reactions such as $CH_2 + CH_3F \rightarrow C_2H_5F^*$ and $C_2H_5 + F_2 \rightarrow C_2H_5F^* + F$ (Kirk et al., 1968). A similar approach by Rabinovitch et al. (1963) provided a microcanonical rate constant for the butyl radical decomposition over a 4 kcal/mol energy range. Agreement with RRKM theory in both cases was noted.

The search for nonrandom energy flow finally succeeded when Rynbrandt and Rabinovitch (1970, 1971a,b) reacted singlet methylene with hexafluorovinylcyclopropane to produce a bi-cyclic excited molecule.



The excited molecule could decompose by ring opening, or it could be stabilized. It was noted that at pressures below about 100 Torr, the two rings opened with nearly equal probability which indicates that the energy initially deposited in the nascent ring has been equilibrated. However, as shown in figure 1.3, above a pressure of about 100 Torr the ring opening was more dominant in the $c-C_3F_3D_2$ ring. The collisional deactivation rate apparently becomes greater than the energy relaxation rate at pressures in excess of 100 Torr. This indicates that in this molecule energy flow between the two cyclopropyl rings takes place with a rate of only $3 \times 10^9 \text{ sec}^{-1}$. This result is not only of historical significance, it also remains today as one of the very few examples of incomplete energy randomization in the dissociation of molecules. In a related chemical activation study involving F plus tetra-allyl tin, Rogers et al. (1982) found that apparently the heavy tin atom located at the center of the molecule prevented rapid energy flow between the allyl units thereby increasing the dissociation rates by a factor of 1000. The most numerous examples of hindered energy flows are found not in normal molecules or ions, but in loosely bound dimers which require typically less than 1000 cm^{-1} to dissociate. The reason for these non RRKM dissociations are discussed fully in chapters 6 and 10.

1.6 TRAJECTORY STUDIES OF UNIMOLECULAR DECOMPOSITION

While the statistical RRKM/QET theory was being used to fit fall-off curves and the results of chemical activation studies, its fundamental assumptions were also being tested by classical trajectory calculations, an approach pioneered by Bunker (1962,

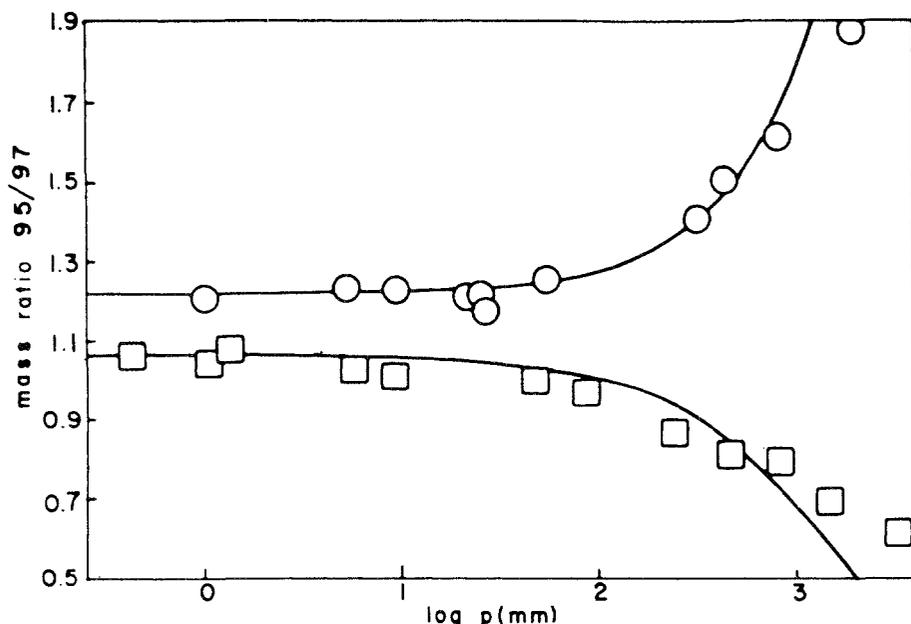


Figure 1.3 Ratio of products from the chemical activation of hexafluorovinylcyclopropane. \circ are for CPO + CD_2 , while \square are for CPO- d_2 + CH_2 . In the mass spectral analysis, the partially fluorinated cyclopropyl rings with m/z 95 ($\text{C}_3\text{F}_3\text{H}_2$) and m/z 97 ($\text{C}_3\text{F}_3\text{D}_2$) were used to identify the ring position after the reaction. The deviation of the m/z 95/97 ratio above 100 Torr pressure indicates that the unactivated ring tended to remain intact. Taken with permission from Rynbrandt and Rabinovitch (1971a).

1964, 1966, 1970) and co-workers (Bunker and Pattengill, 1968; Bunker and Hase, 1973; Harris and Bunker, 1971). If a molecule is excited randomly at constant total energy, so that a microcanonical ensemble of molecular states is prepared, RRKM theory predicts the ensemble will decay exponentially:

$$N(t) = N(0)e^{-k(E)t}, \quad (1.22)$$

where $N(t)$ is the concentration at time t , and $k(E)$ is the RRKM rate constant. The lifetime distribution $P(t)$, which is the probability that decomposition occurs at time t , is given by

$$P(t) = \frac{-1}{N(0)} \frac{dN(t)}{dt}. \quad (1.23)$$

Hence, according to RRKM theory, $P(t)$ is given by

$$P(t) = k(E)e^{-k(E)t}. \quad (1.24)$$

Thus if a molecule's unimolecular decomposition is in accord with RRKM theory, the $t = 0$ intercept of its $P(t)$ will equal $k(E)$, and its $P(t)$ will be exponential with a decay constant equal to $k(E)$ (Bunker, 1966).

Bunker and co-workers (Bunker, 1962, 1964; Bunker and Pattengill, 1968; Harris and Bunker, 1971; Bunker and Hase, 1973) used classical trajectory simulations to study the nature of $P(t)$ for a variety of model molecules. Since the initial states for the

classical trajectories are chosen from a microcanonical ensemble, the $t = 0$ intercept of the trajectory $P(t)$ is the classical RRKM unimolecular rate constant. For this equivalency to be strictly correct, there can be no recrossing of the transition state by the trajectories (Steinfeld et al., 1989) which was shown to be the case for the classical trajectories (Bunker and Pattengill, 1968). The full anharmonicity of the molecule's potential energy surface can be treated in the trajectory simulations, so that a comparison of $k(E)$ determined from the intercept of the trajectory $P(t)$ with $k(E)$ calculated from classical harmonic RRKM theory gives the anharmonic correction to the RRKM rate constant (Bunker and Pattengill, 1968; Bunker, 1970).

For many of the model molecules studied by the trajectory simulations, the decay of $P(t)$ was exponential with a decay constant equal to the RRKM rate constant. However, for some models with widely disparate vibrational frequencies and/or masses, decay was either nonexponential or exponential with a decay constant larger than $k(E)$ determined from the intercept of $P(t)$. This behavior occurs when some of the molecule's vibrational states are inaccessible or only weakly coupled. Thus, a microcanonical ensemble is not maintained during the molecule's decomposition. These studies were a harbinger for what is known now regarding inefficient intramolecular vibrational energy redistribution (IVR) in weakly coupled systems such as van der Waals molecules and mode-specific unimolecular dynamics.

1.7 CONCLUSION

Prior to about 1970, classical experiments, in which the samples were in a thermal heat bath, resulted in an uncertain energy content of the molecule, as well as uncertain collisional deactivation rates. Although RRKM theory provided an excellent framework for a qualitative, as well as semiquantitative, understanding of the unimolecular reactions, the experiments failed to provide firm evidence for the fundamental correctness of the statistical assumptions.

Since 1970, direct photolysis of molecules or ions in low-pressure, collisionless environments, has permitted molecules to be excited to well-defined energy levels, while the use of pulsed lasers or coincidence techniques has provided an accurate external time base with which to measure the dissociation rate constants over many orders of magnitude. It is often the case that more precise experimental results lead to fundamental changes in the theoretical models which describe the phenomena. This has not happened in the case of unimolecular reactions. The statistical theory has remained surprisingly robust. Most molecular systems that dissociate on a bound potential energy surface do so in a statistical fashion. What has changed in the past 25 years is our ability to apply the statistical theory. It is now possible to calculate unimolecular rate constants with essentially no adjustable parameters and which are in quantitative agreement with experiments.

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Vibrational/Rotational Energy Levels

The first step in a unimolecular reaction is the excitation of the reactant molecule's energy levels. Thus, a complete description of the unimolecular reaction requires an understanding of such levels. In this chapter molecular vibrational/rotational levels are considered. The chapter begins with a discussion of the Born-Oppenheimer principle (Eyring, Walter, and Kimball, 1944), which separates electronic motion from vibrational/rotational motion. This is followed by a discussion of classical molecular Hamiltonians, Hamilton's equations of motion, and coordinate systems. Hamiltonians for vibrational, rotational, and vibrational/rotational motion are then discussed. The chapter ends with analyses of energy levels for vibrational/rotational motion.

2.1 BORN-OPPENHEIMER PRINCIPLE

The Born-Oppenheimer principle assumes separation of nuclear and electronic motions in a molecule. The justification in this approximation is that motion of the light electrons is much faster than that of the heavier nuclei, so that electronic and nuclear motions are separable. A formal definition of the Born-Oppenheimer principle can be made by considering the time-independent Schrödinger equation of a molecule, which is of the form

$$\hat{H}\Psi = (\hat{T}_N + \hat{T}_e + V_{NN} + V_{ee} + V_{Ne})\Psi = E\Psi \quad (2.1)$$

where \hat{T}_N is the kinetic energy operator of the nuclei, \hat{T}_e is the kinetic energy operator of the electrons, V_{NN} is the repulsive electrostatic potential energy of the nuclei, V_{ee} is the repulsive electrostatic potential energy of the electrons, and V_{Ne} is the attractive electrostatic potential energy between the nuclei and electrons. The Born-Oppenheimer principle allows one to write the total molecular wave function Ψ as the product of an electronic wave function Ψ_e and a nuclear wave function Ψ_N :

$$\Psi = \Psi_e(R, r) \Psi_N(R), \quad (2.2)$$

where Ψ_e depends on both the nuclear coordinates R and electronic coordinates r , while Ψ_N only depends on the R coordinates. The electronic wave function Ψ_e is a solution to the electronic Schrödinger equation

$$(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne}) \Psi_e(R, r) = E_e(R) \Psi_e(R, r). \quad (2.3)$$

This equation describes the motion of the electrons for a fixed nuclear configuration R and, when solved, gives the electronic energy $E_e(R)$ for that configuration. By varying R , the electronic energy can be determined as a function of the nuclear coordinates. This type of calculation is considered in chapter 3.

The wave function $\Psi_N(R)$ is the solution to the nuclear Schrödinger equation

$$[\hat{T}_N + V_{NN}(R) + E_e(R)] \Psi_N(R) = E \Psi_N(R), \quad (2.4)$$

where $E_e(R)$, the electronic energy versus R , is found from Eq. (2.3). The sum $V_{NN}(R) + E_e(R)$ represents the potential energy $V(R)$ of the nuclei as a function of their coordinates, which is known as the *potential energy surface*. For a nonlinear molecule consisting of N atoms, the potential energy surface depends on $3N - 6$ independent coordinates. An analytic function which represents a potential energy surface is called a *potential energy function*. Substituting $V(R)$ into Eq. (2.4) gives

$$[\hat{T}_N + V(R)] \Psi_N(R) = E \Psi_N(R), \quad (2.5)$$

where the term $[\hat{T}_N + V(R)]$ is the quantum mechanical Hamiltonian operator for the translational, vibrational, and rotational motion of the molecule. Thus, if the center of mass translation motion is removed from the nuclear kinetic energy \hat{T}_N , solving Eq. (2.5) yields the vibrational/rotational energy levels, E , and wave functions, $\Psi_N(R)$, for the molecule (Hirst, 1985). However, before considering such a solution to Eq. (2.5), it is useful to review classical Hamiltonians and coordinate systems for the nuclear motion of a molecule.

2.2 CLASSICAL HAMILTONIANS, HAMILTON'S EQUATIONS OF MOTION, AND COORDINATE SYSTEMS

The classical mechanical energy for the nuclear motion of a molecule is given by the Hamiltonian H (Goldstein, 1950) which depends on the nuclear coordinates \mathbf{q} and their conjugate momenta \mathbf{p} and is a sum of kinetic and potential energies:

$$H = T + V \quad (2.6)$$

This equation is the classical analog of the quantum mechanical operator $\hat{T}_N + V(R)$ in Eq. (2.5). A generalized momentum is defined by

$$p_i = \partial L / \partial \dot{q}_i, \quad (2.7)$$

where L , the Lagrangian, is defined as $L = T - V$.

In laboratory-based Cartesian coordinates T is only a function of the Cartesian momenta and is written as

$$T = \sum_{i=1}^N (\mathbf{p}_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2) / 2m_i \quad (2.8)$$

for a molecule with N atoms. On the other hand, the potential energy V is a function of the Cartesian coordinates. The nuclear motion for the molecule can be determined from H by simultaneously solving Hamilton's equations of motion for each coordinate q_i and its conjugate momentum p_i :

$$\partial q_i / \partial t = \partial H / \partial p_i, \quad \partial p_i / \partial t = -\partial H / \partial q_i \quad (2.9)$$

For laboratory-based Cartesian coordinates the index i extends from 1 to $3N$.

Though the above Hamiltonian in Cartesian momenta and coordinates is certainly

correct, it is not very useful for representing the energy of a molecule since properties of the potential energy are usually not apparent in Cartesian coordinates and the Cartesian kinetic energy expression does not distinguish rotational, vibrational, and coriolis kinetic energies. To represent these chemically more interesting molecular energies, it is necessary to transform from Cartesian coordinates to molecular-type coordinates. In the following, molecular-type coordinates are considered for both diatomic and polyatomic molecules.

2.2.1 Diatomic Molecule

For a diatomic molecule the Cartesian Hamiltonian can be transformed to a Hamiltonian dependent on relative (or internal) and center-of-mass coordinates and momenta. The relative coordinates x, y, z and their conjugate momenta are defined by

$$\begin{aligned} x &\equiv x_2 - x_1, & y &\equiv y_2 - y_1, & z &\equiv z_2 - z_1 \\ p_x &\equiv \mu v_x, & p_y &\equiv \mu v_y, & p_z &\equiv \mu v_z, \end{aligned} \quad (2.10)$$

where $v_x = dx/dt$ and the reduced mass is defined by

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad (2.11)$$

The center-of-mass coordinates and momenta are

$$\begin{aligned} X &\equiv \frac{m_1 x_1 + m_2 x_2}{M}, & Y &\equiv \frac{m_1 y_1 + m_2 y_2}{M}, & Z &\equiv \frac{m_1 z_1 + m_2 z_2}{M}, \\ P_X &\equiv M v_X, & P_Y &\equiv M v_Y, & P_Z &\equiv M v_Z, \end{aligned} \quad (2.12)$$

where $M = m_1 + m_2$. If the diatomic Hamiltonian is expressed in terms of relative and center-of-mass coordinates, it turns out that

$$H = \left[\frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z) \right] + \left[\frac{1}{2M} (P_x^2 + P_y^2 + P_z^2) \right] \quad (2.13)$$

The first term in brackets represents the vibrational/rotational motion of the molecule, while the second term represents the molecule's translational motion; i.e., $H = H_{vr} + H_t$. Since there are no couplings between the two terms, they can be treated separately.

The vibrational/rotational motion of a diatomic molecule can be confined to one plane (e.g., the x, y -plane) and the relative coordinates and momenta in Eq. (2.10) can be transformed to polar coordinates and momenta by the relations

$$\begin{aligned} r &= (x^2 + y^2)^{1/2}, & \theta &= \tan^{-1}(y/x), \\ p_r &= p_x \cos\theta + p_y \sin\theta, \\ p_\theta &= -p_x r \sin\theta + p_y r \cos\theta. \end{aligned} \quad (2.14)$$

Here, p_r and p_θ are the radial and angular momentum. In polar coordinates the diatomic Hamiltonian becomes

$$H = p_r^2/2\mu + p_\theta^2/2\mu r^2 + V(r). \quad (2.15)$$

According to Hamilton's equations of motion, Eq. (2.9), $\partial H/\partial\theta = -\partial p_\theta/\partial t$. Since H is independent of θ , $\partial H/\partial\theta = 0$ and p_θ , the angular momentum, is a constant of the motion. This angular momentum p_θ represents rotation about a Cartesian axis, and it is common practice to use the symbol j for p_θ . The second term in Eq. (2.15), which depends on the angular momentum and the bond length r , is considered the rotational kinetic energy at small r and the centrifugal potential at large r . The concept of a centrifugal barrier is discussed in chapter 7 when considering angular momentum for dissociating molecules.

In a more complete treatment than that given in the preceding paragraph, the vibrational/rotational Hamiltonian in x , y , and z coordinates is transformed to the following vibrational/rotational Hamiltonian in r , θ , and ϕ spherical polar coordinates (Pauling and Wilson, 1935; Davidson, 1962):

$$H = p_r^2/2\mu + p_\theta^2/2\mu r^2 + p_\phi^2/2\mu r^2 \sin^2\theta + V(r). \quad (2.16)$$

The relations between p_r , p_θ , p_ϕ and p_x , p_y , p_z are given in Davidson (1962).

2.2.2 Polyatomic Molecules

To write a Hamiltonian that distinguishes vibrational, rotational, and coriolis kinetic energies for a polyatomic molecule it is necessary to consider figure 2.1, which illustrates the relationship between fixed laboratory-based and rotating center-of-mass-based coordinate systems for a molecule with N atoms (Wilson et al., 1955; Califano, 1976). The instantaneous position of the i th atom in the rotating system is given by a vector \mathbf{r}_i with components x_i , y_i , z_i and the equilibrium position by a vector \mathbf{r}_i^0 with components x_i^0 , y_i^0 , z_i^0 (these latter components are the equilibrium coordinates with

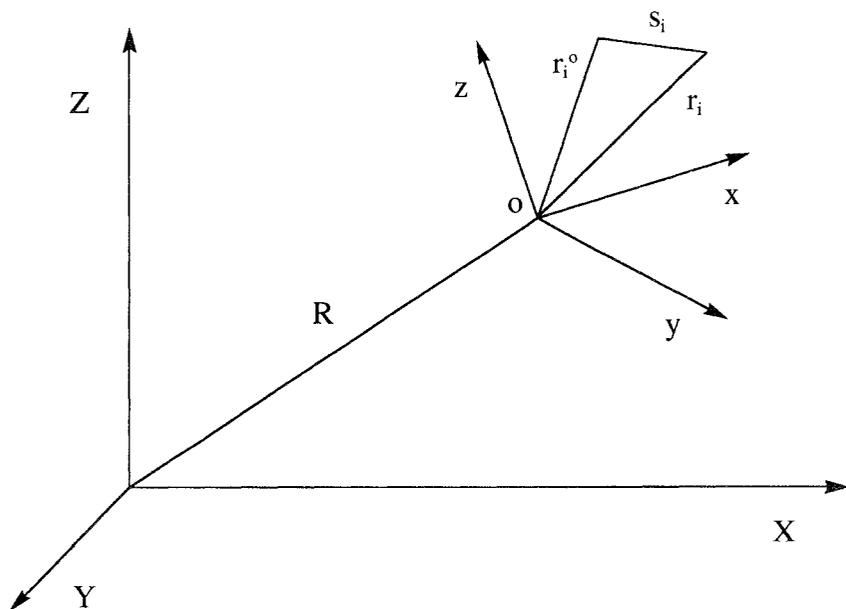


Figure 2.1 Fixed (X , Y , Z) and rotating (x , y , z) axes systems. Taken from Califano (1976).

respect to the rotating system). The instantaneous displacement of the i th atom from its equilibrium position in the rotating system is then given by

$$\mathbf{s}_i = \mathbf{r}_i - \mathbf{r}_i^0. \quad (2.17)$$

The velocity of the i th atom in a molecule with respect to a fixed-laboratory framework can be written as

$$\mathbf{v}_i = \dot{\mathbf{R}} + \boldsymbol{\omega} \times \mathbf{r}_i + \dot{\mathbf{s}}_i, \quad (2.18)$$

where $\dot{\mathbf{R}}$ is the velocity vector of the center of mass and $\boldsymbol{\omega}$ is the angular velocity of the rotating coordinate system attached to the molecule with respect to the fixed-laboratory frame.

The kinetic energy of the molecule is found by summing the kinetic energies of the individual atoms, that is,

$$\begin{aligned} 2T = \sum m_i \mathbf{v}_i \cdot \mathbf{v}_i = & \dot{\mathbf{R}}^2 \sum m_i + \sum m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \sum m_i \dot{\mathbf{s}}_i^2 \\ & + 2\dot{\mathbf{R}} \cdot \boldsymbol{\omega} \times \sum m_i \mathbf{r}_i + 2\dot{\mathbf{R}} \cdot m_i \dot{\mathbf{s}}_i + 2\sum m_i \boldsymbol{\omega} \times \mathbf{r}_i \cdot \dot{\mathbf{s}}_i. \end{aligned} \quad (2.19)$$

The first three terms in Eq. (2.19) represent the pure translational, rotational, and vibrational kinetic energies while the remaining three represent the corresponding interaction energies. From the definition of the center of mass in the rotating frame,

$$\sum_i m_i \mathbf{r}_i = 0. \quad (2.20)$$

By differentiating this equation with respect to time, it follows that

$$\sum_i m_i \dot{\mathbf{r}}_i = \sum_i m_i (\boldsymbol{\omega} \times \mathbf{r}_i + \dot{\mathbf{s}}_i) = \boldsymbol{\omega} \times \sum_i m_i \mathbf{r}_i + \sum_i m_i \dot{\mathbf{s}}_i = \sum_i m_i \dot{\mathbf{s}}_i. \quad (2.21)$$

Equation (2.20) is called the first Sayvetz (or Eckart) condition (Wilson et al., 1955; Califano, 1976) and specifies that during a molecular vibration the center of mass of the molecule remains constant. Introducing Eqs. (2.20) and (2.21) into Eq. (2.19) causes the first two interaction terms to vanish.

The second Sayvetz (or Eckart) condition is chosen so "that whenever the atomic displacements in a molecular vibration tend to produce a rotation of the molecule, the rotating system reorients in order to eliminate this component of the motion" (Califano, 1976). This condition, which is given by

$$\sum m_i \mathbf{r}_i^0 \times \dot{\mathbf{s}}_i = 0, \quad (2.22)$$

means that during a molecular vibration there must be no zero-order vibrational angular momentum. Replacing \mathbf{r}_i by $\mathbf{r}_i^0 + \mathbf{s}_i$ in the last term in Eq. (2.19) and introducing the condition in Eq. (2.22) into this term gives

$$2T = \dot{\mathbf{R}}^2 \sum m_i + \sum m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \sum m_i \dot{\mathbf{s}}_i^2 + 2\boldsymbol{\omega} \cdot \sum (m_i \mathbf{s}_i \times \dot{\mathbf{s}}_i). \quad (2.23)$$

The first term in this equation represents the molecule's center of mass translational motion and can be ignored since it is separable from the other terms. The second and third terms represent the molecule's rotational and vibrational kinetic energies, respec-

tively, and the last term represents the vibrational/rotational coupling often called the coriolis energy.

2.2.2.1 Vibrational motion

2.2.2.1.a *Internal coordinates.* Equation (2.23) is usually the starting point for formulating a molecular vibrational Hamiltonian. If the angular velocity is zero and the center of mass motion ignored, T in Eq. (2.23) becomes $\sum m_i \dot{s}_i^2/2$, the vibrational kinetic energy in molecular-based Cartesian coordinates. It is more meaningful to represent the vibrational energy in curvilinear internal coordinates (such as bond lengths and valence angle bends) than in Cartesian coordinates, and $\sum m_i \dot{s}_i^2/2$ can be transformed without approximation to the following curvilinear coordinate expression for a molecule's vibrational kinetic energy (Wilson et al., 1955):

$$T = \sum_{i,j}^n g_{ij} p_i p_j / 2. \quad (2.24)$$

In this equation the g -elements are effective reduced mass terms, the p_i are the internal coordinate momenta, and n is the number of internal coordinates. The specific value for a g -element depends on the coordinates to which p_i and p_j are conjugate. There are general formulas for the g -elements. A triatomic molecule has two bond lengths and a valence angle bend, and the g -elements for these types of coordinates are listed in table 2.1. As shown in table 2.1, it is common for a g -element to depend on the internal coordinates. Thus, in internal coordinates the kinetic energy depends on the internal coordinates as well as the momenta. Standard trigonometric and vector expressions are used to relate Cartesian and curvilinear internal coordinates, for example, a bond length is $r = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$ and a valence angle bend is $\cos\phi = \mathbf{r}_1 \cdot \mathbf{r}_2 / |r_1| |r_2|$.

An internal coordinate vibrational Hamiltonian is constructed by combining Eq.

Table 2.1. G -elements for a Triatomic Molecule^a

	r_1	r_2	ϕ
r_1	$1/\mu_1^b$	$\cos\phi/M$	$-\sin\phi/Mr_2$
r_2	$\cos\phi/M$	$1/\mu_2$	$-\sin\phi/Mr_1$
ϕ	$-\sin\phi/Mr_2$	$-\sin\phi/Mr_1$	$\frac{1}{m_1 r_1^2} + \frac{1}{m_2 r_2^2} + \frac{1}{M} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} - \frac{2\cos\phi}{r_1 r_2} \right)$

^aThe masses of the molecule are identified as m_2 - M - m_2 . The bond lengths are r_1 and r_2 and ϕ is the valence angle bend.

^b $\mu_1 = m_1 M / (m_1 + M)$.

(2.24) with the potential energy in internal coordinates. Consider a triatomic molecule with coordinates r_1 , r_2 , and ϕ and conjugate momenta p_1 , p_2 , and p_ϕ , for which the g -elements are listed in table 2.1. The internal coordinate vibrational Hamiltonian for this molecule is

$$H = p_1^2/2\mu_1 + p_2^2/2\mu_2 + p_1p_2 \cos\phi/M + A p_\phi^2/2m_1m_2Mr_1^2 r_2^2 - p_1p_\phi \sin\phi/Mr_2 - p_2p_\phi \sin\phi/Mr_1 + V(r_1, r_2, \phi), \quad (2.25)$$

where

$$A = m_1(m_2 + M)r_1^2 + m_2(m_1 + M)r_2^2 - 2m_1m_2r_1r_2 \cos\phi, \quad (2.26)$$

$\mu_1 = m_1M/(m_1 + M)$, $\mu_2 = m_2M/(m_2 + M)$, the masses m_1 and M are separated by r_1 , the masses m_2 and M are separated by r_2 , and ϕ is the m_1 - M - m_2 bond angle. If one wishes to consider only the two stretching coordinates, $\sin\phi$ is set to its fixed value in the Hamiltonian (e.g., zero for a linear molecule) and p_ϕ is set to zero. One of the strengths of representing vibrational motion with an internal coordinate Hamiltonian is that it is straightforward to include all the coupling in the potential energy. However, as illustrated by Eqs. (2.24) and (2.25) there is also kinetic (i.e., momenta) coupling in the Hamiltonian. A more general approach for constructing a Hamiltonian with constrained coordinates is described by Hadder and Frederick (1992).

2.2.2.1.b Normal mode coordinates. Either the Cartesian coordinate or internal coordinate vibrational Hamiltonian can be transformed to a normal mode Hamiltonian by assuming infinitesimal displacements for the Cartesian (or internal) coordinates from the equilibrium geometry. Here, following Califano (1976), the transformation between Cartesian and normal mode coordinates is illustrated. Instead of using molecular-based Cartesian displacement coordinates s_i , Eq. (2.17), it is convenient to use mass-weighted Cartesian displacement coordinates which are defined by

$$q_i = \sqrt{m_i} s_i. \quad (2.27)$$

The kinetic energy can then be expressed in the simpler form

$$2T = \sum_{i=1}^{3N} \dot{q}_i^2 \quad (2.28)$$

For small displacements from the equilibrium geometry, the potential energy can be represented by the power series

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + 1/2 \sum_{ij} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots \quad (2.29)$$

and without loss of generality, the potential energy can be shifted so that the minimum of the potential V_0 is zero. By definition, a potential energy minimum requires

$$\left(\frac{\partial V}{\partial q_i} \right)_0 = 0 \quad (2.30)$$

for each of the coordinates. For sufficiently small displacements of the coordinates it is only necessary to retain the quadratic terms in Eq. (2.29), so that the potential becomes

$$2V = \sum_{i,j} f_{ij} q_i q_j, \quad (2.31)$$

where the force constants f_{ij} are given by

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0. \quad (2.32)$$

Note, that since q is in mass-weighted coordinates, the units of the force constants f_{ij} are simply sec^{-2} , rather than the usual $\text{kg}\text{-sec}^{-2}$. A potential which only includes quadratic terms is called a *harmonic potential*. *Anharmonicity* arises from the higher-order terms.

The expressions for T , Eq. (2.28), and V , Eq. (2.31), can be written in a simpler form using matrix notation. Using the column vector \mathbf{q} , whose components are the $3N$ mass-weighted Cartesian displacement coordinates,

$$2T = \dot{\mathbf{q}} \dot{\mathbf{q}} \quad (2.33)$$

and

$$2V = \tilde{\mathbf{q}} \mathbf{F} \mathbf{q}, \quad (2.34)$$

where the symbol \sim denotes the transpose vector and \mathbf{F} is a $3N \times 3N$ real symmetric matrix of the force constants f_{ij} , Eq. (2.32); that is, \mathbf{F} is a hermitian matrix. The F matrix is not diagonal since it contains all possible nondiagonal cross terms. However, it is interesting to consider the effect of a diagonal \mathbf{F} matrix. For such a situation the vibrational energy could be expressed as the sum $E = \sum E_i$, where E_i would equal $(\dot{q}_i^2 + f_{ii} q_i^2)/2$. Though such a solution is not obtained for Cartesian coordinates, it is worthwhile to ask whether the energy becomes separable at small displacements for another coordinate system.

Equation (2.24) shows that, because of the kinetic energy coupling, in internal coordinates the energy is not separable at small displacements. Thus, it is necessary to search for $3N$ new coordinates Q_k called *normal mode coordinates*, which define a new column vector \mathbf{Q} . To begin it will be assumed that the mass-weighted Cartesian coordinates and normal mode coordinates are related by a linear transformation of the form

$$Q_k = \sum_i l'_{ki} q_i. \quad (2.35)$$

In matrix notation this transformation is written as

$$\mathbf{Q} = \mathbf{L}^{-1} \mathbf{q}, \quad (2.36)$$

where the l'_{ki} are the components of \mathbf{L}^{-1} . The reverse transformation is written as

$$\mathbf{q} = \mathbf{L} \mathbf{Q} \quad (2.37)$$

where \mathbf{L} is the inverse of \mathbf{L}^{-1} and $\mathbf{L} \mathbf{L}^{-1}$ equals the unit matrix \mathbf{E} . In the following it is shown that this linear transformation gives the desired solution. To solve the normal

mode problem in internal coordinates, such a linear transformation is made between internal and normal mode coordinates. However, in general these internal coordinates are not the curvilinear internal coordinates described in the previous section, but are rectilinear internal coordinates (Califano, 1976). These two types of internal coordinates are only the same for infinitesimal displacements.

For the energy to be separable in normal mode coordinates requires both the kinetic and potential energies to be diagonal; that is,

$$2T = \tilde{\mathbf{Q}} \dot{\mathbf{Q}} \quad (2.38)$$

and

$$2V = \tilde{\mathbf{Q}} \mathbf{\Lambda} \mathbf{Q}, \quad (2.39)$$

where $\mathbf{\Lambda}$ is a diagonal matrix with elements λ_k . Requiring both Eqs. (2.38) and (2.39) to be satisfied simultaneously allows one to determine both \mathbf{L} and $\mathbf{\Lambda}$. Inserting Eq. (2.37) into Eq. (2.33) gives

$$2T = \tilde{\mathbf{Q}} \tilde{\mathbf{L}} \mathbf{L} \dot{\mathbf{Q}} \quad (2.40)$$

and comparison with Eq. (2.38) shows that

$$\tilde{\mathbf{L}} \mathbf{L} = \mathbf{E}. \quad (2.41)$$

Thus, an important property of \mathbf{L} is that it is orthogonal since

$$\tilde{\mathbf{L}} = \mathbf{L}^{-1}. \quad (2.42)$$

Similarly, inserting Eq. (2.37) into Eq. (2.34) gives

$$2V = \tilde{\mathbf{Q}} \tilde{\mathbf{L}} \mathbf{F} \mathbf{L} \mathbf{Q}, \quad (2.43)$$

and a comparison with Eq. (2.39) shows that

$$\tilde{\mathbf{L}} \mathbf{F} \mathbf{L} = \mathbf{\Lambda}. \quad (2.44)$$

Thus, another important property of \mathbf{L} is that it diagonalizes the force constant matrix. Also, since \mathbf{L} is an orthogonal matrix, Eq. (2.44) can be written in the form of a general eigenvalue equation, that is,

$$(\mathbf{F} - \mathbf{\Lambda})\mathbf{L} = \mathbf{0}. \quad (2.45)$$

Solving Eq. (2.45) is a standard problem in linear algebra [an example solution is outlined in Steinfeld et al. (1989)]. The solution gives $\mathbf{\Lambda}$, which is a diagonal matrix of the $3N$ eigenvalues λ_k and the eigenvector matrix \mathbf{L} with components l_{ik} , which define the transformation between normal mode coordinates Q_k and the mass-weighted Cartesian displacement coordinates q_i , that is,

$$q_i = \sum_k l_{ik} Q_k. \quad (2.46)$$

Thus, the l_{ik} in Eq. (2.46) are one of the $3N$ rows of \mathbf{L} while the l'_{ik} in Eq. (2.35) are one of the $3N$ columns. For a nonlinear molecule there are six zero eigenvalues in $\mathbf{\Lambda}$, which correspond to translation and external rotation motions. The remaining $3N - 6$ nonzero eigenvalues equal $4\pi^2\nu_k^2$, where the ν_k 's are the normal mode vibrational frequencies.

A numerical solution to Eq. (2.45) for the H₂O molecule is given in table 2.2. The calculation was performed for a potential which has an OH quadratic stretching force constant of 7.60 mdyn/Å and a HOH quadratic bending force constant of 0.644 mdyn-Å/rad². These internal force constants are transformed to Cartesian force constants by writing the internal coordinates as functions of Cartesian coordinates as described above, following Eq. (2.24). This is a standard procedure and is used in the general dynamics computer program VENUS (Hase et al., 1996). The first six eigenvalues in table 2.2, which are for translation and rotation are only approximately zero, since the solution is obtained numerically. If the solution were obtained analytically, these six eigenvalues would be exactly zero. The remaining three eigenvalues, with frequencies of 1595, 3662, and 3716 cm⁻¹ are for the three normal modes of vibration. Sketching the eigenvectors for these normal modes shows they are a symmetric bend, a symmetric stretch and an asymmetric stretch, respectively.

The normal mode Hamiltonian is the sum of Eqs. (2.38) and (2.39), and can be written as

$$H = \sum_k (P_k^2 + \lambda_k Q_k^2)/2, \quad (2.47)$$

where the definition of the generalized momentum, Eq. (2.7), has been used to replace \dot{Q}_k with P_k . Solving Hamilton's equations of motion, Eq. (2.9), for the normal mode Hamiltonian confirms that $\lambda_k = 4\pi^2\nu_k^2$. Equation (2.47) is strictly valid only for small coordinate displacements, since only the quadratic (i.e., harmonic) potential is retained in its derivation. Because the inclusion of anharmonicity in the potential energy does not affect the kinetic energy in the normal mode Hamiltonian, the anharmonic vibrational energy in normal mode coordinates is written as

$$H = \sum_i (P_i^2 + \lambda_i Q_i^2)/2 + V_{\text{anh}}(Q_1, Q_2, \dots), \quad (2.48)$$

where V_{anh} is the anharmonic contribution to the potential expanded in higher order terms (cubic, quartic, etc.). However, in treating highly vibrationally excited molecules, one often expresses the Hamiltonian in internal coordinates instead of normal mode coordinates, since it is usually much more difficult to represent an anharmonic potential in normal mode coordinates than in curvilinear internal coordinates. Equations (2.47) and (2.48) are incomplete in that they do not include the term for vibrational angular momentum (Wilson and Howard, 1936; Darling and Dennison, 1940; Carney et al., 1978; Romanowski et al., 1985). As shown in the following section, this term is a component of the normal mode Hamiltonian even if the total rotational angular momentum of the molecule is zero.

A normal mode analysis can also be performed in curvilinear internal coordinates (Wilson et al., 1955). The approach is the same as that described above for Cartesian coordinates with one major modification. In an internal coordinate normal mode analysis, the internal coordinate cannot be simply scaled by the masses as is done for the Cartesian coordinates, Eq. (2.27), so that the masses become an explicit part of the eigenvalue problem. Thus, in an internal coordinate normal mode analysis, one does not solve Eq. (2.45), but instead solves the eigenvalue equation

$$(\mathbf{G}\mathbf{F} - \mathbf{\Lambda})\mathbf{L} = 0, \quad (2.49)$$

Table 2.2. Normal Mode Frequencies and Eigenvectors for H₂O.^a

	1.450 ^b	0.1168 <i>i</i>	0.0016	0.0350	2.671	2.947	1595	3662	3716
<i>x</i> _O	0.0436 ^c	0.0000	0.0000	0.2367	0.0000	0.0000	0.0000	0.0000	-0.0676
<i>y</i> _O	0.0000	0.0033	0.2356	0.0000	0.0000	0.0000	-0.0639	-0.0540	0.0000
<i>z</i> _O	0.0000	0.2321	-0.0032	0.0000	0.0000	-0.0929	0.0000	0.0000	0.0000
<i>x</i> _{H1}	-0.3968	0.0000	0.0000	0.2261	0.0000	0.0000	-0.4544	0.5381	0.5362
<i>y</i> _{H1}	0.5688	0.0033	0.2356	0.0137	0.0000	0.0000	0.5071	0.4282	0.4152
<i>z</i> _{H1}	0.0000	0.2617	-0.0036	0.0000	0.7043	0.6539	0.0000	0.0000	0.0000
<i>x</i> _{H2}	-0.3968	0.0000	0.0000	0.2261	0.0000	0.0000	0.4544	-0.5381	0.5362
<i>y</i> _{H2}	-0.5688	0.0033	0.2356	-0.0137	0.0000	0.0000	0.5071	0.4282	-0.4152
<i>z</i> _{H2}	0.0000	0.2617	-0.0036	0.0000	-0.7043	0.6539	0.0000	0.0000	0.0000

^aEq. (2.45) is solved numerically to find the frequencies and eigenvectors. H₂O is in the *x,y*-plane with the O-atom at the origin. The *x,y*-coordinates for the H-atoms are (-0.75669, -0.58589) for H1 and (0.75669, -0.58589) for H2.

^bThe first eigenvalue, where $\nu_i = \sqrt{\lambda_i}/2\pi$. ν_i is in cm⁻¹.

^cThe eigenvector for the first eigenvalue.

where \mathbf{F} is a matrix of the internal coordinate force constants and \mathbf{G} is a matrix of the internal coordinate g -elements, Eq. (2.24) and table 2.1, which represent the masses. The \mathbf{L} -matrix gives the transformation between normal mode and internal coordinates, as in Eqs. (2.36) and (2.37) where the q are now internal coordinates. In contrast to force constants for Cartesian coordinates, internal coordinate force constants are of chemical significance since they pertain to particular motions of a molecule. Nondiagonal internal coordinate force constants are often called "interaction terms," since they describe how the displacement of a particular internal coordinate affects the potential of the remaining coordinates. Internal coordinate quadratic force constants for H_2O and CH_4 are listed in table 2.3. The internal coordinates are depicted in figure 2.2. The nondiagonal force constants are $f_{r\bar{r}}$, $f_{r\alpha}$, and $f_{r\alpha'}$. For the latter force constant, the bond length r is not for one of the bonds which define the bend angle α' .

2.2.2.2 Rotation and vibrational/rotational motion

The simplest approach for treating the rotational motion of a molecule is to make the rigid-rotor approximation so that the third and fourth terms in Eq. (2.23) are zero. In Cartesian coordinates the second term becomes

$$T_r = \sum_{i=x,y,z} j_i^2/2I_i, \quad (2.50)$$

where the I_i are the principal moments of inertia and the j_i are the angular momenta about the Cartesian axes. The rotational Hamiltonian can also be expressed using Eulerian angles (Wilson et al., 1955), but the resulting Hamiltonian depends on whether the molecule is a spherical, symmetric, or asymmetric top. For a symmetric top the Hamiltonian is

$$T_r = \frac{p_\theta^2}{2I_A} + \frac{(p_\phi - p_\psi \cos\theta)^2}{2I_A \sin^2\theta} + \frac{p_\psi^2}{2I_C}, \quad (2.51)$$

where I_A , I_A and I_C are the three principal moments of inertia, and θ , ϕ , and ψ are the three Euler angles, with the ranges $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, $0 \leq \psi \leq 2\pi$.

If the total angular momentum of the molecule is not zero, all of the terms in Eq.

Table 2.3. Internal Coordinate Force Constants for H_2O and CH_4 .^a

	H_2O^b	CH_4^c
rr	8.454	5.422
$r\bar{r}$	-0.101	0.0038
$\alpha\alpha$	0.761	0.5848
$r\alpha$	0.228	0.183
$r\alpha'$	—	-0.186

^a rr and $r\bar{r}$ force constants are in mdyn/Å, $r\alpha$, and $r\alpha'$ in mdyn/rad, and $\alpha\alpha$ in mdyn-Å/rad².

^bB.J. Rosenberg et al. (1976).

^cR.J. Duchovic et al. (1984).

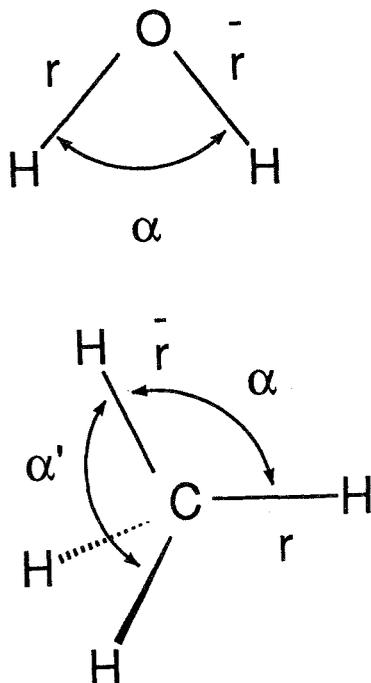


Figure 2.2 Internal coordinates for H_2O and CH_4 .

(2.23) must be included in an exact calculation of simultaneous vibrational/rotational motion. Transforming the Hamiltonian in Eq. (2.23) which is for a Cartesian rotating coordinate system to a Hamiltonian of rotating internal or normal mode coordinates is a considerable task. The vibrational/rotational Hamiltonian in terms of normal mode coordinates and a rotating body-fixed axes system, chosen in accord with the Eckart (Sayvetz) conditions described above, is often called the Watson Hamiltonian (Wilson and Howard, 1936; Watson, 1968b, 1970) and is written as

$$H = \sum_k (P_k^2 + \lambda_k Q_k^2)/2 + V_{\text{anh}}(Q_1, Q_2, \dots) \quad (2.52)$$

$$+ \sum_{\alpha, \beta} (j_\alpha - \pi_\alpha) \mu_{\alpha\beta} (j_\beta - \pi_\beta)/2,$$

where $\alpha(\beta) = x, y,$ or z -axis, $\mu_{\alpha, \beta}$ is a component of the inverse effective moment of inertia tensor, j_α is the component of the total rotational angular momentum along the body-fixed α -axis, and π_α is the vibrational angular momentum along the α -axis which gives rise to coriolis coupling. There are two types of vibration/rotation couplings in Eq. (2.52) (Herzberg, 1945). Centrifugal coupling occurs through the coordinate dependence of the $\mu_{\alpha\beta}$ tensor. Even if the coordinate dependence of $\mu_{\alpha\beta}$ is ignored, coriolis coupling arises through the cross term $-\sum_{\alpha, \beta} \mu_{\alpha\beta} j_\alpha \pi_\beta$. If these coupling

terms are removed by neglecting π_α and setting the $\mu_{\alpha\beta}$ to their values at the equilibrium geometry, the third term in Eq. (2.52) becomes equal to Eq. (2.50). This becomes apparent if the moment of inertia tensor is diagonalized, so that the nondiagonal $\mu_{\alpha\beta}$

are zero and the diagonal terms, for example, $\mu_{\alpha\alpha}$, are simply inverses of the principal moments of inertia. It is noteworthy that if the total angular momentum j equals zero, the vibrational angular momentum still contributes to the Hamiltonian through the $\pi_{\alpha}\mu_{\alpha\beta}\pi_{\beta}/2$ terms. The utility of the Watson Hamiltonian is that it has a simple expression for vibrational and rotational kinetic energy, with vibrational/rotational coupling terms which are of physical significance. Its drawback is the often exceedingly complicated expression for the anharmonic potential energy in normal mode coordinates.

The anharmonic potential energy is usually easier to represent in internal coordinates than in normal mode coordinates. However, what restricts the use of internal coordinates is the complicated expression for the vibrational/rotational kinetic energy in these coordinates (Pickett, 1972). It is difficult to write a general expression for the vibrational/rotational kinetic energy in internal coordinates and, instead, one usually considers Hamiltonians for specific molecules. For a bent triatomic molecule confined to rotate in a plane, the internal coordinate Hamiltonian is (Blais and Bunker, 1962):

$$\begin{aligned} H_{vr} = & T_v - p_1 p_\theta \sin\phi/2Mr_2 + p_2 p_\theta \sin\phi/2Mr_1 \\ & + [m_1(m_2 + M)r_1^2 - m_2(m_1 + M)r_2^2]p_\phi p_\theta/2m_1 m_2 Mr_1^2 r_2^2 \\ & + [A + 4m_1 m_2 r_1 r_2 \cos\phi]p_\theta^2/8m_1 m_2 Mr_1^2 r_2^2 + V(r_1, r_2, \phi) \end{aligned} \quad (2.53)$$

where T_v is the vibrational kinetic energy from Eq. (2.25), A is given in Eq. (2.26), and p_θ is the angular momentum. Equation (2.53) shows that p_θ couples with both the internal coordinates and momenta. The second, third, and fourth terms couple the internal coordinate momenta p_1 , p_2 , and p_ϕ with the rotational angular momentum. If the molecule were allowed to rotate about all three of its axes, many additional coupling terms would be added to Eq. (2.53). Internal coordinate Hamiltonians have been presented for three and four atoms with complete three-dimensional vibrational/rotational coupling (Bramley et al., 1991; Bramley and Handy, 1993). In comparing Eqs. (2.52) and (2.53), the physical picture of vibration/rotation coupling is different for the internal coordinate and normal mode Hamiltonians, and cannot be described in terms of coriolis and centrifugal couplings when using the internal coordinate Hamiltonian. Finally, since the coordinate θ does not appear explicitly in Eq. (2.53), p_θ is a constant of the motion. (The angular variable θ is measured from a fixed reference line in the plane in which the molecule is rotating.)

2.3 ENERGY LEVELS

Vibrational, rotational, and vibrational/rotational energy levels are found by first transforming the classical Hamiltonians described in the previous section to the appropriate quantum mechanical operator \hat{H} . The eigenvalue equation

$$\hat{H}\psi = E\psi \quad (2.54)$$

is then solved to obtain the energy levels and corresponding wave functions. In the following, solutions to Eq. (2.54) are described for both diatomic and polyatomic molecules

2.3.1 Diatomic Molecule

If p_θ in Eq. (2.15) is set equal to zero, the Hamiltonian represents just the vibrational energy for the diatomic molecule. The quantum mechanical Hamiltonian operator for this vibrational motion is

$$\hat{H} = \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V(r) \quad (2.55)$$

and the eigenvalue equation, Eq. (2.54), must be solved to find the vibrational energy levels. In general analytic solutions are not obtained. However, both the harmonic oscillator potential

$$V(r) = f \Delta r^2/2 \quad (2.56)$$

and anharmonic Morse potential

$$V(r) = D[1 - e^{-\beta\Delta r}]^2 \quad (2.57)$$

give analytic expressions for the energy levels. The force constant f , bond dissociation energy D and exponential term β are related by $f = 2D\beta^2$. For the harmonic oscillator the energy levels are given by

$$E_n = (n + \frac{1}{2}) h\nu_e, \quad (2.58)$$

where $n = 0, 1, 2, \dots$ and ν_e , the harmonic vibrational frequency, is $(f/\mu)^{1/2}/2\pi$. The energy levels for the Morse potential are

$$E_n = (n + 1/2) h\nu_e - (n + \frac{1}{2})^2 h\nu_e\chi_e, \quad (2.59)$$

where $\nu_e = \beta(2D/\mu)^{1/2}/2\pi$ and $\chi_e = h\nu_e/4D$.

Rigid-rotor rotational energy levels are found from the Hamiltonian in Eq. (2.15) by fixing r at the equilibrium bond length $r = r_e$ so that H becomes $p_\theta^2/2\mu r_e^2$. Transforming H to the Hamiltonian operator for rotational motion and solving Eq. (2.54) gives

$$E_J = J(J + 1)/\hbar^2/2I_e \quad (2.60)$$

for the rotational energy levels, where the quantum number $J = 0, 1, 2, \dots$, the moment of inertia I_e equals μr_e^2 and each level has a $2J + 1$ degeneracy. Combining either Eq. (2.58) or (2.59) with Eq. (2.60) gives approximate harmonic and anharmonic vibrational/rotational energy levels for the diatomic molecule, respectively. Since the actual moment of inertia changes as the molecule vibrates (i.e., r changes), a more accurate expression includes *vibrational/rotational coupling*. Also, the rotational motion of the molecule causes the bond to stretch, a *centrifugal distortion* effect. Using second-order perturbation theory to include such terms, yields the following expression for the anharmonic vibrational/rotational energy levels:

$$\begin{aligned} E_{nj} = & (n + \frac{1}{2}) h\nu_e - (n + \frac{1}{2})^2 h\nu_e\chi_e + J(J + 1)\hbar^2/2I_e \\ & - h\alpha_e(n + \frac{1}{2})J(J + 1) - h C_e J^2(J + 1)^2. \end{aligned} \quad (2.61)$$

The fourth and fifth terms in this expression represent the vibrational/rotational coupling and the centrifugal distortion, respectively.

2.3.2 Polyatomic Molecules

2.3.2.1 Vibrational energy levels

The Hamiltonian operator for the normal mode Hamiltonian in Eq. (2.47) is obtained by replacing P_k with the operator $-i\hbar \partial/\partial Q_k$. Hence

$$\hat{H}_v = \sum_k \left(\frac{-\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{\lambda_k}{2} Q_k^2 \right). \quad (2.62)$$

Solving the eigenvalue equation, Eq. (2.54), for this operator gives the normal mode energy levels

$$E_v = \sum_i (n_i + 1/2) h\nu_i \quad (2.63)$$

and wave function

$$\psi = \prod_i \chi_i(n_i) \quad (2.64)$$

which is a product of harmonic oscillator wave functions for the individual normal modes. Equations (2.63) and (2.64) are valid at low total energies, so that the vibrational Hamiltonian is nearly separable in normal mode coordinates and the vibrational wave functions are well approximated by the product of normal mode wave functions. Thus, one can associate specific structural attributes to an energy level and assign the level names such as stretching, bending, rocking, etc. Each ψ has a different probability amplitude (given by ψ^2) on the potential energy surface. The states have easily identifiable spectral patterns and progressions which are evident to any trained spectroscopist.

In table 2.4, a comparison is made between harmonic and anharmonic frequencies determined for C_2H_4 from experiment. The anharmonic frequencies, which are given by the $n = 0 \rightarrow 1$ transitions for the vibrational modes, are 2–4% smaller than the harmonic frequencies. This small error is typical for molecules at low vibrational energies. However, for more highly excited vibrational levels the accuracy of the normal mode model decreases.

At higher levels of excitation anharmonicity has to be included to obtain accurate energy levels. Perturbation theory has been used to derive the following expression, often called a Dunham expansion (Hirst, 1985), for polyatomic anharmonic vibrational energy levels, which is similar to the Morse energy level expression Eq. (2.59), for a diatomic molecule:

$$E(\text{cm}^{-1}) = \sum_i \omega_i(n_i + \frac{1}{2}) + \sum_i \sum_{k \geq i} x_{ik}(n_i + \frac{1}{2})(n_k + \frac{1}{2}) \quad (2.65)$$

This equation assumes there are individual vibrational modes with identifiable quantum numbers n_i , vibrational frequencies ω_i , and anharmonicities x_{ik} for an excited molecule, in the same way quantum numbers and vibrational frequencies can be

Table 2.4. Experimental Harmonic and Anharmonic Vibrational Frequencies for C_2H_4 .^a

	Harmonic	Anharmonic
ν_1	3152	3026
ν_2	1655	1630
ν_3	1370	1342
ν_4	1044	1023
ν_5	3232	3103
ν_6	1245	1220
ν_7	969	949
ν_8	959	940
ν_9	3234	3105
ν_{10}	843	826
ν_{11}	3147	3021
ν_{12}	1473	1444

^aThe frequencies are in cm^{-1} and are taken from Duncan et al. (1973).

assigned to modes in the normal mode model; that is, Eqs. (2.63) and (2.64). However, at higher energies this equation may not fit the vibrational energy levels (Reisner et al., 1984; Abramson et al., 1985), and another approach is needed for calculating the energy levels.

The variational method (Carney et al., 1978) is a general approach for calculating vibrational energy levels. The wave function for a vibrational energy level Ψ_n is written as a linear combination of basis function ψ_i ,

$$\Psi_n = \sum_i c_{in} \psi_i \quad (2.66)$$

The energies and wave functions for the energy levels are calculated by requiring the energy,

$$\int \Psi_n^* \hat{H}_v \Psi_n d\tau / \int \Psi_n^* \Psi_n d\tau, \quad (2.67)$$

to be stationary with respect to the variational parameters c_{in} , which gives an upper limit to the energy. This gives rise to a set of homogeneous simultaneous equations, secular equations, which involve the following integrals over the basis functions:

$$H_{ij} = \int \psi_i \hat{H}_v \psi_j d\tau. \quad (2.68)$$

If an exact vibrational Hamiltonian is used (e.g., either the internal coordinate, Eq. (2.25), or normal mode, Eq. (2.52) Hamiltonian), the accuracy of the calculated results only depends on the treatment of anharmonicity in the potential energy function. The variational calculation is not restricted to a particular type of basis functions; for example, either normal mode or internal coordinate bases can be used. However, one wants to choose a basis which simplifies the evaluation of the integrals in Eq. (2.68). Thus, if the calculations are performed with the normal mode Hamiltonian, a normal mode basis is preferred. Normal mode and internal coordinate basis sets are usually

centered at the molecule's equilibrium geometry. In recent work Bačić and Light, 1986; Bačić and Light, 1989; Choi and Light, 1992) a discrete variable representation, DVR, basis has been advanced for calculating vibrational energy levels. This is a particularly useful approach for treating large-amplitude motion. Whatever basis set is used, its size is increased until the calculated vibrational energy levels converge to within a fixed criterion; for example, 0.01 cm^{-1} .

If there is a principal ψ_i in the linear combination, Eq. (2.66), which gives the wave function Ψ_n for the energy level, the quantum numbers for this ψ_i define the "almost good" quantum numbers for Ψ_n . For example, at low levels of excitation, where the vibrational Hamiltonian is nearly separable in normal mode coordinates and forms a good zero-order Hamiltonian, there will be only one principal normal mode basis function in the linear combination. However, at higher levels of excitation where anharmonic couplings between the normal mode coordinates become possible, there may not be one principal normal mode basis function in ψ_n . As a result, it may be impossible to assign normal mode quantum numbers to the energy levels. If this is the case it is useful to determine whether basis functions associated with another type of zero-order Hamiltonian, would give assignable wave functions. (Note, if bases of sufficient size are used, changing the basis functions for the calculation will not affect the calculated energy levels, but will alter the coefficients c_{in} , Eq. (2.66), for the energy level's wave function). If there is no zero-order Hamiltonian and associated basis functions which yield one principal ψ_i for each Ψ_n , the vibrational energy levels are said to be *intrinsically unassignable*. In the last section of this chapter the concept of intrinsic unassignability is discussed in terms of regular and irregular spectra.

The result of a variational calculation of the formyl radical HCO vibrational energy levels is given in table 2.5 (Cho et al., 1990). An internal coordinate Hamiltonian and internal coordinate basis functions were used in this calculations. The bases

Table 2.5. Variational Calculation of Vibrational States for the Formyl Radical.

Energy, cm^{-1}	Wave Function ^a
2815.13	-0.9962 000> +0.0506 110> +0.0424 100>
3896.22	0.9808 001> +0.1462 010> -0.0784 101>
4689.41	0.9803 010> -0.1477 001> -0.0690 120>
4966.72	-0.9579 002> -0.1986 011> +0.1140 102>
5227.70	0.9670 100> -0.1531 200> +0.1134 002>
5767.13	-0.9411 011> -0.2085 020> +0.1982 002>
6025.14	0.9216 003> +0.2297 012> +0.2129 101>
6245.86	0.9196 101> -0.2167 003> -0.2123 201>
6537.25	0.9638 020> -0.2095 011> -0.0814 130>
6833.82	-0.8966 012> -0.2789 021> +0.2277 003>
7068.20	0.8479 004> +0.3427 102> +0.2389 013>
7090.64	0.9134 110> -0.1543 210> -0.1483 200>
7220.80	0.7504 200> +0.3868 102> -0.2676 300>
7267.20	0.7451 102> -0.4210 200> -0.2810 004>
7611.67	0.8996 021> -0.2767 012> +0.2575 030>

^aResults are for a calculation with a $10 \times 9 \times 10 = 900$ basis set. The largest three coefficients in the eigenvector are listed. The notation $|n_1 n_2 n_3\rangle$ indicates n_1 quanta in the H—C stretch mode, n_2 quanta in the C=O stretch mode, and n_3 quanta in the H—C=O bending mode. Calculations by Cho et al. (1990).

consists of Morse stretch basis functions for the first 10 C—H stretch internal coordinate energy levels, Morse stretch basis functions for the first 9 C=O stretch internal coordinate energy levels, and harmonic basis functions for the first 10 H—C=O bend energy levels. For the lowest energy (zero-point) level the coefficient is -0.9962 for the $|000\rangle$ basis function. The most highly mixed levels are at 7090.6 and 7267.2 cm^{-1} . Quantum numbers can be assigned to each of the levels. A survey of vibrational variational calculations for different molecules is given in table 2.6.

2.3.2.2 Rotational and vibrational/rotational energy levels

To determine the quantum mechanical rigid-rotor energy levels, the quantum mechanical Hamiltonian operator is formed from the classical Hamiltonian in Eq. (2.50) and the eigenvalue equation, Eq. (2.54), is solved. For a symmetric top rigid-rotor, which has two equal moments of inertia (i.e., $I_a = I_b \neq I_c$), the resulting energy levels are

$$E_{J,K} = [J(J+1) - K^2]\hbar^2/2I_a + K^2\hbar^2/2I_c, \quad (2.69)$$

where $J = 0, 1, 2, \dots$ and $K = -J, -(J-1), \dots, 0, \dots, J-1, J$. For “almost symmetric tops” which have $I_a \approx I_b$, one can often use the approximation (Townes and Schalow, 1955)

$$E_{J,K} = \left(\frac{1}{I_a} + \frac{1}{I_b}\right) \frac{[J(J+1) - K^2]\hbar^2}{4} + \frac{K^2\hbar^2}{2I_c}. \quad (2.70)$$

Approximate vibrational/rotational energy levels for symmetric top and “almost symmetric top” molecules are found by combining Eq. (2.65) with either Eq. (2.69) or Eq. (2.70). This approach is incomplete since it neglects vibrational/rotational coupling and centrifugal distortion, which for a diatomic are the fourth and fifth terms in Eq. (2.61). Using perturbation theory, Watson (1968a) has derived an analytic expression for the vibrational/rotational levels of a polyatomic molecule (Toselli and Barker, 1989). The expression includes anharmonic, coriolis, and centrifugal distortion terms and expresses the energy in terms of the vibrational quantum numbers n_i and the

Table 2.6. Variational Calculations of Vibrational and Vibrational-Rotational Energy Levels.

Molecule	Hamiltonian	Levels	Reference
H ₂ O	Radau	Vib.	Choi and Light (1992)
SO ₂ , H ₂ CO	Internal Coordinate ^a	Vib.-Rot.	McCoy et al. (1991)
LiCN/LiNC	Jacobi	Vib.	Bačić and Light (1986)
HCN/HNC	Jacobi	Vib.	Bačić and Light (1987)
KCN	Jacobi	Vib.-Rot.	Tennyson and Sutcliffe (1982)
H ₂ CO	Watson	Vib.-Rot.	Maessen and Wolfsberg (1985)
CH ₃ F	Normal Mode	Vib.	Dunn et al. (1987)
H ₂ CO	Watson	Vib.	Romanowski et al. (1985)
H ₂ CO	Watson	Vib.	Maessen and Wolfsberg (1984)
HCO	Internal Coordinate	Vib.	Cho et al. (1990)
HCO	Watson	Vib.	Bowman et al. (1986)
C ₂ H ₂	Internal Coordinate	Vib.	McCoy and Sibert (1991)
C ₂ H ₂	Internal Coordinate	Vib.	Bramley and Handy (1993)
C ₂ H ₂	Internal Coordinate	Vib.	Sibert and Mayrhofer (1993)

^aCanonical Van Vleck perturbation theory and variational calculation.

rotational quantum numbers J and K . However, even this expression breaks down at sufficiently high energy and angular momentum, because it does not include all anharmonic and vibrational/rotational coupling terms.

Vibration/rotation energy levels can always be determined with the use of variational procedures. In this approach the wave function Ψ_J for a given vibration-rotation level is written as a linear combination of basis functions $\psi_i R_{JK}$

$$\Psi_J = \sum_i \sum_K c_{iK}^J \psi_i R_{JK}, \quad (2.71)$$

where ψ_i is a suitable vibrational wave function (e.g., the normal mode wave function in Eq. (2.64)), R_{JK} is a symmetric top wave function, and c_{iK}^J is a variational parameter. Vibrational/rotational coupling will mix the $(2J + 1)K$ -levels for a particular J . If this coupling is extensive so that all K -levels are mixed, K will no longer be a meaningful quantum number for an energy level. Variational calculations of vibrational/rotational energy levels for several molecules have provided insight into the importance of K -mixing and its relationship to anharmonic coupling (McCoy et al., 1991; Burleigh and Sibert, 1993).

As discussed above, anharmonic coupling in the potential can make it impossible to assign vibrational quantum numbers to an energy level. Thus, at levels of excitation where there is extensive anharmonic and vibrational/rotational coupling it may only be possible to identify an energy level by its energy (i.e., position in the spectrum) and its total angular momentum J . However, regardless of the assignability or unassignability of the energy levels, below the unimolecular threshold the spectrum is discrete, with individual lines only broadened by their coupling with the radiation field.

2.3.3 Semiclassical Calculation of Vibrational/Rotational Energy Levels

Another approach for finding vibrational energy levels is to apply the semiclassical quantization condition to classical trajectories determined by solving Hamilton's equations of motion, Eq. (2.9). This approach originates from critical insights by Einstein (1917) and is usually referred to as Einstein-Brillouin-Keller (EBK) semiclassical quantization (Percival, 1977; Noid et al., 1981). It can be derived by either applying quantization conditions to classical mechanics or by taking the Wentzel-Kramers-Brillouin (WKB) semiclassical limit of quantum mechanics (Schiff, 1968). For a diatomic molecule with no angular momentum, so that H in Eq. (2.15) becomes $H = p_r^2/2\mu + V(r)$, the semiclassical quantization condition is that $\oint p_r dr$ integrated over one vibrational period is $(n + \frac{1}{2})h$, where n is an integer and equals 0, 1, 2, A more convenient notation for this condition is

$$\oint p_r dr = (n + \frac{1}{2})h, \quad (2.72)$$

where the cyclic integral denotes integration over one period (i.e., orbit). The integral on the left side of Eq. (2.72) is called the action integral. The fraction $\frac{1}{2}$ in Eq. (2.72), is the Maslov index and is found by a detailed semiclassical study of the classical motion (Gutzwiller, 1990). Orbits for harmonic oscillator energy levels, Eq. (2.58), are shown in figure 2.3.

To find the semiclassical vibrational energy levels for a diatomic, Eq. (2.72) is written as