

William R. Moomaw¹
and James F. Skinner
Williams College
Williamstown, Massachusetts 01267

Vibronic Spectra and Energy Levels of Polyatomic Molecules

A physical chemistry experiment

Quantum mechanics and its application to chemical problems has become an integral part of many undergraduate curricula and is treated in a number of excellent, recent texts (1-3). It is our observation, however, that unless students work directly with the properties of real systems, elementary quantum mechanics, with its emphasis on artificial but soluble problems remains simply another area of abstract knowledge. We have found that the analysis and assignment of spectra which the student has measured is very helpful in increasing his understanding of many quantum mechanical concepts.

A number of spectroscopic experiments have been reported in THIS JOURNAL including the analysis of the vibrational and rotational spectra of simple molecules (4-6), the electronic band spectra of diatomic molecules (7, 8), and the electronic spectra of aromatic molecules in condensed media (9, 10). The recent article by Hollenberg (11) contains a useful general discussion of the relationship between molecular states and molecular spectroscopy.

In the experiment described below the student measures and assigns the vapor phase vibronic (vibrational-electronic) spectrum of an aromatic and an azaaromatic molecule. The vibrational assignments in the ground and excited states are made on the basis of a comparison with the infrared and Raman spectra, and an energy level diagram is constructed. To understand the relationship between the measured spectrum and the energy level diagram, the student is introduced to the concepts of one-electron orbitals and energies, state energies, normal coordinate displacements, fundamental and overtone frequencies in the harmonic oscillator approximation, combination frequencies, the Born-Oppenheimer approximation, and the Franck-Condon principle. Different aspects of these analyses have been used successfully in our third-year experimental methods course and in our fourth-year quantum chemistry course.

Theory

The motions of the N atomic nuclei of a molecule are conveniently described in terms of three translations, three rotations (two for linear molecules), and $3N - 6$ vibrations ($3N - 5$ for linear molecules). Because of the limited resolution of the spectrometer used in this experiment, only changes in the vibrational energy will

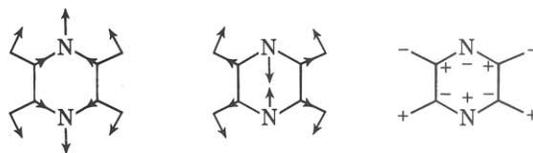
be observed to accompany electronic transitions. We shall therefore ignore the rotations, and describe the molecule in terms of a simple Born-Oppenheimer state function which assumes the separability of the electronic and nuclear motions (12)

$$\psi(q, Q) = \psi_e(q, Q)\psi_v(Q) \quad (1)$$

The vibrational state function, ψ_v , depends only upon nuclear coordinates, Q , whereas the electronic state function, ψ_e , depends on electronic coordinates, q , and parametrically on the nuclear coordinates. The independence of the electronic and nuclear motions implies that the electronic energy, E_e , and the vibrational energy, E_v , will simply add to give the total energy of a particular vibronic state

$$E = E_e + E_v \quad (2)$$

Each of the $3N - 6$ vibrations in a polyatomic molecule may be described in terms of displacements along normal coordinates of the molecule. It is found that for a single vibrational mode, each atom in the molecule moves in a definite phase relationship to every other atom, and that this complex motion is described by a single frequency (13). Three of the modes active in the lowest electronic transition of pyrazine are shown below with their vibrational frequencies in the ground ($\bar{\nu}''$) and excited ($\bar{\nu}'$) electronic states (14, 15).



$\bar{\nu}'' = 596 \text{ cm}^{-1}$	$\bar{\nu}'' = 1230 \text{ cm}^{-1}$	$\bar{\nu}'' = 919 \text{ cm}^{-1}$
$\bar{\nu}' = 582 \text{ cm}^{-1}$	$\bar{\nu}' = 1162 \text{ cm}^{-1}$	$\bar{\nu}' = 383 \text{ cm}^{-1}$
CC in plane	CH in plane	CH out of plane

The vibrational energy states for each of these complicated modes are found to be nearly equally spaced, and so may be described by the same simple one-dimensional harmonic oscillator expression that is used for diatomic molecules (11). Hence for the n th vibrational mode

$$E_{v_n} = \left(v_n + \frac{1}{2} \right) h\nu_n \quad v_n = 0, 1, 2, 3, \dots \quad (3)$$

where v_n is the value of the vibrational quantum number for the n th vibrational mode, ν_n is its fundamental frequency, and h is Planck's constant. If the vibrational modes are independent of each other, then the total vibrational energy of the molecule will be the sum of the energies of the individual vibrational modes. Hence,

¹To whom correspondence should be directed. A more detailed discussion of the theoretical background for this experiment, suitable for students, is available from the authors.

the energy of the molecule in the ground electronic state will be

$$E'' = E_e'' + \sum_{n=1}^{3N-6} \left(v_n'' + \frac{1}{2} \right) h\nu_n'' \quad (4)$$

and the energy of the molecule in the excited state will be

$$E' = E_e' + \sum_{m=1}^{3N-6} \left(v_m' + \frac{1}{2} \right) h\nu_m' \quad (5)$$

Note that when all the quantum numbers are equal to zero, the pure electronic energy still includes the sum of the zero point vibrational energies, $\frac{1}{2} h\nu$.

When a transition occurs between two vibronic levels, the change in energy of the molecule will be

$$\Delta E = E_e' - E_e'' + \sum_{m=1}^{3N-6} \left(v_m' + \frac{1}{2} \right) h\nu_m' - \sum_{n=1}^{3N-6} \left(v_n'' + \frac{1}{2} \right) h\nu_n'' \quad (6)$$

or in terms of wavenumbers

$$\Delta E = \bar{\nu} = \bar{\nu}_{00} + \sum_{m=1}^{3N-6} \sum_{n=1}^{3N-6} (v_m' \bar{\nu}_m' - v_n'' \bar{\nu}_n'') \quad (7)$$

The vibrational zero point energy has been incorporated in the electronic terms, the symbol $\bar{\nu}_{00}$ being used to denote the transition between the zero vibrational level of one electronic state and the zero level of the other, i.e., when all the vibrational quantum numbers are zero. This transition is often referred to as the zero-zero ($0' \leftarrow 0''$) or pure electronic transition even though it contains the difference in the vibrational zero point energies. Of course each of the vibrational quantum numbers, v_n'' and v_m' , will have to be specified for all of the $3N - 6$ vibrational modes in both the ground and excited states to describe the energy difference for a single vibronic transition, giving rise to a single vibronic band in the spectrum.

Let us now examine specifically the kinds of transitions that may occur in absorption when various vibrations are excited during an electronic promotion. To simplify our discussion, let us first consider the possibility that only one of the $3N - 6$ normal vibrations, say the l th mode, can change its energy or quantum number during the electronic excitation, while all other modes remain unchanged ($v_i' \leftarrow v_i''$, all other $v_m' = v_n'' = 0$). The ground state molecules will not all have the same amount of vibrational energy; some will be vibrationally unexcited ($v_l'' = 0$), while others as the result of collisions will have one or more quanta of vibrational energy ($v_l'' = 1$, or 2, or 3, or any integer). It is convenient to think of all the molecules that have the same vibrational energy (same value of v_l'') as a distinct "chemical" species. Collisions between these different species may interconvert them, and at high enough pressures (a few torr) they are in fact in equilibrium. The equilibrium constant, K , which relates the concentrations, $M_{v_l''(r)}$ and $M_{v_l''(s)}$ of two species characterized by different quantum numbers $v_l''(r)$ and $v_l''(s)$ will be the Boltzmann factor

$$K = M_{v_l''(r)} / M_{v_l''(s)} = \exp[-(E_{v_l''(r)} - E_{v_l''(s)}) / kT] \quad (8)$$

where k is Boltzmann's constant and T is the absolute

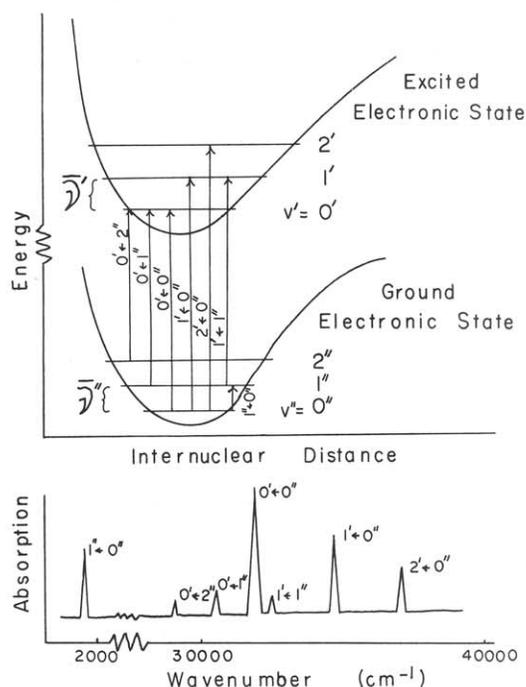


Figure 1. Vibronic transitions and schematic bands. The $1'' \leftarrow 0''$ infrared transition is shown for comparison.

temperature. At room temperature, $kT \cong 210 \text{ cm}^{-1}$, and since the energy differences between vibrational states in organic molecules are from two to twenty times this energy, the vast majority of molecules will be those for which $v_l'' = 0$. Therefore, most of the absorption intensity will result from these $v_l'' = 0$ molecules undergoing transitions to the various excited vibronic states characterized by v_l' . One usually finds a progression of fairly strong absorption bands approximately equally spaced, which begin with the transition $0_l' \leftarrow 0''$, and continue to higher energy as $1_l' \leftarrow 0''$, $2_l' \leftarrow 0''$, $3_l' \leftarrow 0'' \dots v_l' \leftarrow 0''$. This is schematically illustrated in Figure 1. These bands are separated by $\bar{\nu}_l'$, the energy of the excited state fundamental.

The absorption bands resulting from molecules initially in other vibrational levels ($v_l'' > 0$) will also be observed. The concentration of these molecules increases exponentially with temperature (see eqn. (8)), and since the probability of a transition is directly proportional to the concentration of molecules in the initial state, the absorption intensity will increase exponentially with temperature. For this reason the absorption bands arising from vibrationally excited molecules are called "hot bands," and their temperature dependence may be used to identify them. The hot bands will always involve ground state vibrational frequencies which may be correlated with the infrared and Raman spectra, e.g. $0' \leftarrow 1_l''$, $0' \leftarrow 2_l''$, $0' \leftarrow 3_l'' \dots$, or the bands $1_l' \leftarrow 1_l''$, $2_l' \leftarrow 2_l''$, $v_l'(s) \leftarrow v_l''(s)$ which measure the difference between the ground and excited state frequencies (see Fig. 1). The intensities of the bands will of course decrease as v_l'' increases. In practice it is easier to analyze the hot bands on the low energy side of the $0' \leftarrow 0''$ band because of their low intensity relative to the bands arising from molecules for which $v_l'' = 0$.

Of course the actual situation in a polyatomic molecule is much more complicated than that described since there is not just one vibrational frequency that

Table 1. Types of Vibronic Transitions in Absorption

$0' \leftarrow 0''$ $v' = v'' = 0$ for all vibrational modes $1' \leftarrow 0'', 2' \leftarrow 0'', 3' \leftarrow 0'' \dots$ All $v' = v'' = 0$ except for j th vibrational mode	Pure electronic transition. Progression in one vibrational frequency characteristic of excited electronic state. Found to high energy side of $(0' \leftarrow 0'')$.
$1_i' + 1_j' \leftarrow 0'', 2_i' + 1_j' \leftarrow 0''$ \dots All $v' = v'' = 0$ except for i th and j th vibrational modes $0' \leftarrow 1_j'', 0' \leftarrow 2_j'', 0' \leftarrow 3_j''$ \dots All $v' = v'' = 0$ except for j th vibrational mode	Combination band. Simultaneous excitation of two vibrational modes, each independently. Hot band progression in ground state vibrational frequency of the j th mode. Found to low energy side of $(0' \leftarrow 0'')$.
$0' \leftarrow 1_j'', 1_i'' \leftarrow 1_j'', 2_i' \leftarrow 1_j''$ All $v' = v'' = 0$ except i th and j th vibrational modes	Hot band progression in one vibrational frequency characteristic of excited electronic state.
$1_j' \leftarrow 1_j'', 2_j' \leftarrow 2_j'', v_j' \leftarrow v_j''$ All $v' = v'' = 0$ except for j th vibrational mode.	Difference band. Transition within a vibrationally excited molecule in which there is no change in v . Separation from $(0' \leftarrow 0'')$ band depends on $(\bar{\nu}' - \bar{\nu}'')$. See eqn. (7).
$1_i' + 1_j' \leftarrow 1_j'', 2_i' + 1_j' \leftarrow 1_j'' \dots$	Progressions in an excited state frequency in combination with another excited state vibration arising from a ground state molecule having one vibration excited by one quantum.

can appear in the spectrum, but $3N - 6$. For pyrazine, this means 24 vibrations and for chlorobenzene, 30. Therefore, one might expect to see 30 transitions from the vibrationless ground state of chlorobenzene to an excited electronic state in which one of the 30 vibrations was excited by only one quantum ($1' \leftarrow 0''$). Each of these transitions would be only the first in a progression of excited state frequencies. Hence the major part of the absorption spectrum is expected to consist of many progressions in several different excited state frequencies. It is also possible for combination frequencies to appear in which two vibrations are simultaneously excited during the transition (see Table 1 and Fig. 2).

Let us consider the possible number of hot bands we might expect from the thirty different species of ground electronic state molecules having only one quantum of vibrational energy ($v_i'' = 1$, all other $v'' = 0$). Each of these molecules can undergo a transition to the excited electronic state with no vibrations excited (all

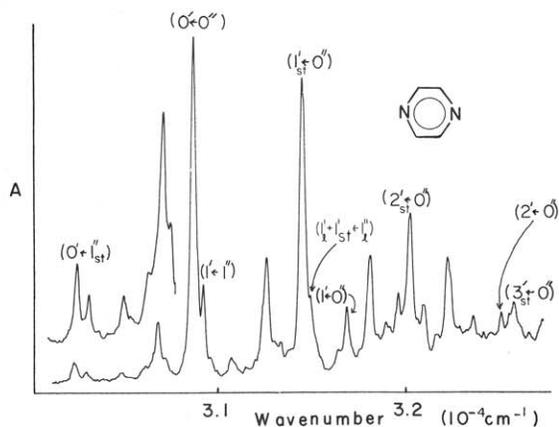


Figure 2. $\pi^* \leftarrow n$ transition for pyrazine vapor.

$v' = 0$), giving rise to 30 bands, or to each of the 30 different states in which only one of the excited state vibrations is excited by one quantum resulting in an additional 900 bands. Each of these bands is only the first member of a progression in excited state frequencies (see Table 1).

Before we give up in despair at the hopelessness of analyzing such a potentially complex spectrum, let us look at some actual examples (Figs. 2 and 3) and be reassured that the number of relatively strong absorption bands is not all that large. To understand why the large number of possible vibronic bands does not appear in the spectrum, one must look at the form of the transition probability expression, P (12). Using Born-Oppenheimer wave functions for the ground (ψ'') and excited (ψ') states

$$P \propto \left[\int_{-\infty}^{\infty} \psi_e'(q, \bar{Q}) \hat{M}(q) \psi_e''(q, \bar{Q}) d\tau_q \int_{-\infty}^{\infty} \psi'_{v_m'}(Q) \psi''_{v_n''}(Q) d\tau_Q \right]^2 \quad (9)$$

where $\hat{M}(q)$ is the transition moment operator. The first integral, called the electronic transition moment integral, is evaluated at the average value of the nuclear coordinates, \bar{Q} , and determines the transition probability between electronic states ψ_e' and ψ_e'' . The second integral is called the Franck-Condon overlap integral and determines the probability that the transition will occur between particular vibrations characterized by quantum numbers v_m' and v_n'' . It is found that the Franck-Condon factors for many of these transitions vanish identically or are very small, so that not all possible transitions between vibronic states will be observed. Furthermore, the magnitude of the non-vanishing Franck-Condon integrals determines the relative intensities of the vibronic bands which do appear.

Before proceeding to the detailed analysis of the lowest energy electronic transitions of pyrazine and chlorobenzene, a word is in order about the types of electronic transitions that are involved. In chlorobenzene, as in benzene itself, three electronic transitions are observed in the near ultraviolet (4000–1850 Å). These correspond to three transitions in which electrons are promoted from filled π (bonding) orbitals to empty π^* (antibonding) orbitals on the benzene ring (16). The energies of these transitions (17), 39,200 cm^{-1} (2550 Å)

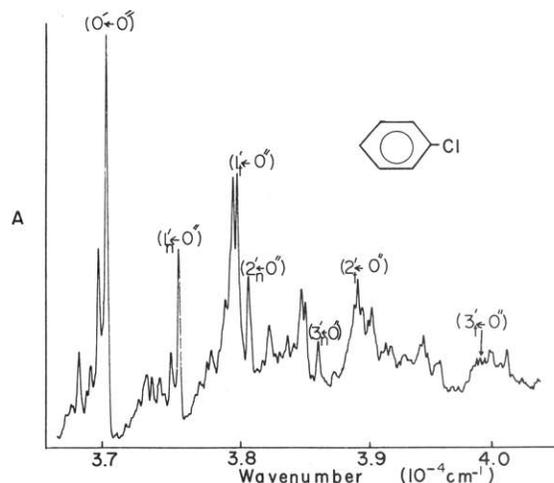


Figure 3. $\pi^* \leftarrow \pi$ transition for chlorobenzene vapor.

48,800 cm^{-1} (2050 Å), and 54,600 cm^{-1} (1830 Å), are very close to those of benzene (18). In pyrazine, transitions similar to those of chlorobenzene are found at 38,763 cm^{-1} (2580 Å), 50,880 cm^{-1} (1965 Å), and 60,700 cm^{-1} (1650 Å), and a new transition at 30,876 cm^{-1} (3238 Å) is also observed (18). This new transition corresponds to the promotion of one of the nonbonding (n -electrons) to the lowest energy π^* orbital (16).

These assignments are based in part upon theoretical considerations (16) and in part upon the solvent shift behavior of the absorption bands. Both $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions are shifted to lower energy relative to the vapor when a molecule is solvated, but the particular behavior of these bands is quite different in polar and nonpolar solvents. It is found that polar or hydrogen bonding solvents shift $\pi^* \leftarrow \pi$ transitions to lower energy than do nonpolar solvents, but shift $\pi^* \leftarrow n$ transitions to higher energy (see Fig. 4). An explana-

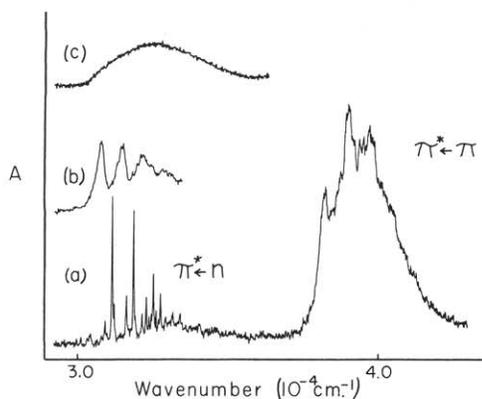


Figure 4. Vibronic spectra of pyrazine: (a) vapor, (b) in cyclohexane, and (c) in methanol.

tion for this behavior is given elsewhere (16). Figure 4 also shows the broadening of the vibronic bands that takes place upon solvation (note the complete loss of vibrational structure in methanol) as a result of the inequivalent solvent environments in which the solute molecules are situated. Because of this solvent broadening, it is the spectrum of the vapor, where band widths are determined by the unresolved rotational structure, that will be analyzed.

Experimental

The procedural details followed in this experiment will be determined by the spectrophotometers used, and therefore only an outline will be given here. The vibronic absorption spectra illustrated below were recorded on a Cary 14 spectrophotometer at room temperature (except Fig. 5) in 1-cm or 10-cm silica cells. The infrared spectrum (Fig. 6) was recorded on a Perkin-Elmer 237B spectrophotometer. Best available grade pyrazine (Aldrich) and chlorobenzene (Eastman) were the substances studied, and, like the spectrograde sol-

² The instructor may wish to substitute other absorbing substances or solvents. The large energy separation between the $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions in pyrazine makes it suitable. The infrared activity of many of the chlorobenzene vibrational modes makes possible the comparison of several $\bar{\nu}''$ values determined from the infrared and vibronic hot bands. The $0' \leftarrow 0''$ band is clearly visible for both of these compounds whereas in benzene, another illustrative example, the $0' \leftarrow 0''$ band is absent.

vents cyclohexane and methanol, were used as received.²

The vapor spectra may be obtained by placing a drop of chlorobenzene or a small crystal of the volatile pyrazine in a capped 1-cm cell. If the absorbance is too great, vapor may be removed from the cell by gently pumping on the cell with a vacuum pump until the condensed phase is removed and an amount of vapor sufficient to bring the most intense band on scale is present. The solutions are best prepared by adding the appropriate solvent directly to the vapor-containing absorption cell.

The hot bands may be most simply recorded by placing a drop of chlorobenzene or a small crystal of pyrazine into a 10-cm cell, heating it to about 100°C in an oven and then rapidly scanning the spectrum. More elaborate sample thermostats could be used. As a result of the low symmetry of chlorobenzene most of the vibrational modes are infrared active and may be correlated with the vibronic hot bands. In pyrazine, however, the intense vibronic hot bands correspond to infrared inactive modes, but most of these vibrational frequencies may be determined from the Raman spectrum.

Precise indication of wavelength must be made on the

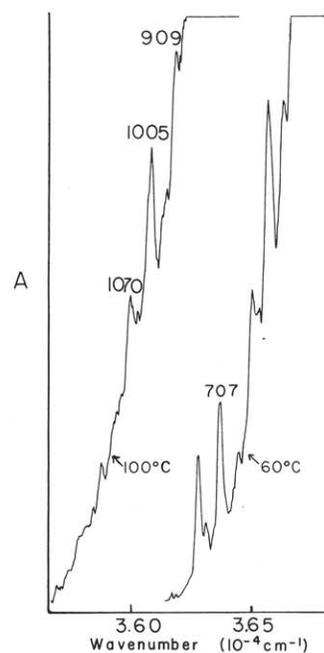


Figure 5. Hot bands for chlorobenzene vapor. The spectrum below 36,200 cm^{-1} was recorded at approximately 100°C while the spectrum above 36,200 cm^{-1} was recorded at approximately 60°C.

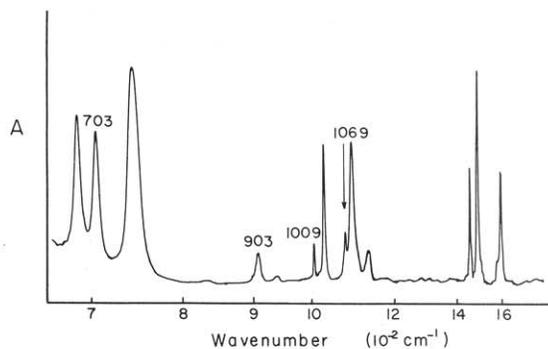


Figure 6. Infrared spectrum of liquid chlorobenzene.

spectra as recorded. With a good ruler, the student then carefully determines (within 1–2 Å) the wavelengths of about 20 prominent bands in the vapor spectrum. Identification of the $0' \leftarrow 0''$ band must be made by inspection or by reference to the literature. The wavelengths are converted to wavenumbers and the wavenumber differences between the $0' \leftarrow 0''$ band and the bands to the *high energy side* of it are determined. This repetitive calculation is readily accomplished using a computer. One then looks for repeating intervals in the list of differences, i.e., $\bar{\nu}'$, $2\bar{\nu}'$, $3\bar{\nu}'$. . . from the $0' \leftarrow 0''$ band. This can be done for both chlorobenzene (17) and pyrazine (15, 19) and reference to the literature will facilitate the analyses. Combination bands will also be observed.

In the hot band analysis of chlorobenzene, the wavenumber differences between the $0' \leftarrow 0''$ band and all prominent peaks to the *low energy side* of it must be calculated. The student must then correlate these differences with values of ground state fundamental vibrational frequencies, $\bar{\nu}''$, directly observed in the infrared spectra.

Discussion

Only the more obvious aspects of each spectrum will be discussed, while literature references to the complete analyses are given for further study. For our students the extent of the analysis was left up to the individual student making the experiment very open-ended.

Let us first consider the pyrazine molecule. Both $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions are observed in this compound (Fig. 4) with the former occurring near 31,000 cm^{-1} . The entire group of sharp bands between 31,000–33,000 cm^{-1} constitutes this $\pi^* \leftarrow n$ transition. An expanded recording of this transition is shown in Figure 2 with the $0' \leftarrow 0''$ band indicated (15, 19). The pyrazine spectrum is characterized by one very prominent high energy progression: the bands labeled ($1_{s'l'} \leftarrow 0''$), ($2_{s'l'} \leftarrow 0''$), and ($3_{s'l'} \leftarrow 0''$) are found to be higher in energy than the $0' \leftarrow 0''$ band by about 584, 2×584 , 3×584 cm^{-1} , respectively. The value, 584 cm^{-1} , corresponds to $\bar{\nu}'$, for a totally symmetric ring stretching vibrational mode (15). The decrease in intensity along this progression is related to the Franck-Condon overlap integral between the two vibronic states involved. The bands labeled ($1' \leftarrow 0''$) and ($2' \leftarrow 0''$) constitute a progression in $\bar{\nu}' = 823$ cm^{-1} . The assignment of this frequency to a particular vibration has not yet been made, and the ground state frequency is unknown.

The band labeled ($1' \leftarrow 1''$) in Figure 2 is separated from the $0' \leftarrow 0''$ band by only 58 cm^{-1} which is too small to be a vibrational frequency. It is assigned to a hot band difference of the type ($\bar{\nu}_{i'} \leftarrow \bar{\nu}_i''$). The combination band designated as $1_{i'} + 1_{s'l'} \leftarrow 1_i''$ corresponds to a ground state molecule with $\nu_i'' = 1$ which retains that vibrational energy during electronic excitation ($\nu_{i'} = 1$) and simultaneously undergoes excitation of a second mode by one quantum ($\nu_{s'l'} = 1$). The band appears $(584 + 58)$ cm^{-1} to the high energy side of the $0' \leftarrow 0''$ band.

The band labeled ($0' \leftarrow 1_{s'l}''$) in Figure 2 is another hot band, 596 cm^{-1} to the low energy side of the ($0' \leftarrow 0''$) band. This value corresponds to the vibrational frequency in the ground electronic state, $\bar{\nu}''$, for the

same pyrazine ring stretching mode to which the value 584 cm^{-1} was assigned for $\bar{\nu}'$. The difference of 12 cm^{-1} is a result of the different vibrational force constants caused by the different electronic distributions in the two electronic states. An observed Raman band at 598 cm^{-1} in liquid pyrazine has been assigned to $\bar{\nu}''$ for this mode (15). Many of the remaining bands can be assigned to combinations of single vibrational frequencies and a progression of the 584 cm^{-1} mode. A partial energy level diagram (drawn to scale) showing two of the twenty-four vibrations is presented in Figure 7.

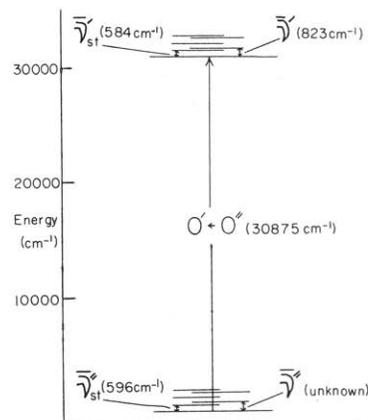


Figure 7. Partial vibronic energy level diagram for pyrazine.

Table 2. Fundamental Vibrational Frequencies ($\bar{\nu}''$) for Chlorobenzene

Infrared		Vibronic Hot Bands	
Student	Reference (20)	Student	Reference (17)
703 cm^{-1}	701 cm^{-1}	707 cm^{-1}	707 cm^{-1}
903		909	907
1009	1002	1005	1004
1069	1068	1070	1064

Let us now consider Figure 3 which shows the lowest energy $\pi^* \leftarrow \pi$ transition for chlorobenzene vapor at room temperature. Transitions from the nonbonding chlorine orbitals to the π^* orbitals on the ring occur at much higher energy. Two progressions in excited state vibrational frequencies, $\bar{\nu}'$, are shown: the one designated with a subscript l is assigned to a totally symmetric ring stretching mode ($\bar{\nu}' = 931$ cm^{-1}) while the one designated with a subscript n is assigned to a nontotally symmetric ring stretch ($\bar{\nu}' = 521$ cm^{-1}). Further analysis may be made by reference to the work of Sponer and Wollman (17).

Figure 5 shows two different portions of the chlorobenzene hot band spectrum. The energy differences (in cm^{-1}) between the $0' \leftarrow 0''$ band (now off scale) and certain of the hot bands are given. These values must be correlated with ground electronic state vibrational frequencies, $\bar{\nu}''$, as determined directly from the infrared spectrum (Fig. 6).

Table 2 compares typical student values of the fundamental vibrational frequencies determined from the hot bands and directly from the infrared spectrum with corresponding literature values.

Literature Cited

- (1) HAMEKA, H. F., "Introduction to Quantum Theory," Harper and Row, New York, 1967.
- (2) HANNA, M. W., "Quantum Mechanics in Chemistry," W. A. Benjamin, New York, 1965.
- (3) ANDERSON, J. M., "Introduction to Quantum Chemistry," W. A. Benjamin, New York, 1969.
- (4) STAFFORD, F. E., HOLT, C. W., AND PAULSON, C. L., *J. CHEM. EDUC.*, **40**, 245 (1963).
- (5) RICHARDS, L. W., *J. CHEM. EDUC.*, **43**, 644 (1966).
- (6) BOOBYER, G. J., AND COX, A. P., *J. CHEM. EDUC.*, **45**, 18 (1968).
- (7) STAFFORD, F. E., *J. CHEM. EDUC.*, **39**, 626 (1962).
- (8) DAVIES, M., *J. CHEM. EDUC.*, **28**, 474 (1951).
- (9) STEVENSON, P. E., *J. CHEM. EDUC.*, **41**, 234 (1964).
- (10) JAFFÉ, H. H., BEVERIDGE, D. L., AND ORCHIN, M., *J. CHEM. EDUC.*, **44**, 383 (1967).
- (11) HOLLENBERG, J. L., *J. CHEM. EDUC.*, **47**, 2 (1970).
- (12) HERZBERG, G., "Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton, New Jersey, 1950.
- (13) BARROW, G. M., "Introduction to Molecular Spectroscopy," McGraw Hill, New York, 1962.
- (14) LORD, R. C., MARSTON, A. L., AND MILLER, F. A., *Spectrochim Acta*, **9**, 113 (1957).
- (15) INNES, K. K., BYRNE, J. P., AND ROSS, I. G., *J. Mol. Spect.*, **22**, 125 (1967).
- (16) MURRELL, J. N., "The Theory of the Electronic Spectra of Organic Molecules," John Wiley & Sons, Inc., New York, 1963.
- (17) SPONER, H., AND WOLLMAN, S. H., *J. Chem. Phys.*, **9**, 816 (1941).
- (18) HERZBERG, G., "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Princeton, New Jersey, 1966.
- (19) ITO, M., SHIMADA, R., KURAIKI, T., AND MIZUSHIMA, W., *J. Chem. Phys.*, **26**, 1508 (1957).
- (20) PLYLER, E. K., ALLEN, H. D., JR., AND TIDWELL, E. D., *J. Res. Nat. Bur. Stan.*, **58**, 255 (1957).

