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THE SEMIRIGID BENDER MODEL AND COMPLETE INTERNAL ROTATION
OF HCN INTO CNH.

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A thesis
submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

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Carleton University

Ottawa, Canada

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ABSTRACT

This thesis is concerned with the calculation of the vibration rotation energy levels, and associated spectra, of a triatomic molecule ABC in which "internal rotation" (really large amplitude bending) ABC--BCA, can occur. The semirigid bender model that was used [P. R. Bunker and D. J. Howe, *J. Mol. Spectrosc.* 83, 288-303 (1980)] has been extended by allowing for the effect of stretching-vibration averaging. The computer programme appropriate for this model has been completely rewritten in such a way as to allow the direct least squares fitting of the *physically meaningful parameters* now appearing in the model to experimentally observed frequencies.

A least squares fitting of all available experimental vibrational data for the $\tilde{X}$ 'A' ground electronic state of HCN/CNH has resulted in the determination of the "true" bending potential function (*i.e.* corrected for stretching vibration averaging) for the internal isomerization HCN--CNH. The variation of the harmonic stretching frequencies with respect to the bending angle has also been determined.

A least squares fitting of the pure bending levels of the $\tilde{A}$ 'A' excited state of HCN/CNH has resulted in the determi-

nation of the "effective" potential function (*i.e.* not corrected for stretching vibration averaging) for internal isomerization in this electronic state.

The wavefunctions obtained from these studies have been used to calculate the relative intensities of different vibrational bands in the $\bar{A}-\bar{X}$ electronic band system of HCN and CNH. The calculated intensities for absorption by HCN were compared with the observed intensities of Herzberg and Innes [*Canad. J. Phys.* 35, 842-879 (1957)] to establish the reliability of this technique and thus of the predicted intensities for absorption by CNH.

By combining such intensity factors with Franck-Condon factors calculated for the C-N stretching vibration, and then convoluting with a Lorentzian line shape instrument function, simulated low resolution emission spectra were obtained. To establish the reliability of the predicted CNH spectrum the simulated HCN spectra were compared to the experimental spectra of A. P. Baranavski [*Chem. Phys. Lett.* 61, 532-537 (1979)].

"Straight-through" calculations, based on *ab initio* values for the parameters of the potential functions, were done to determine the vibrational structures of two other molecules which may undergo internal isomerization: $\text{HCO}^+/\text{COH}^+$ and $\text{HNN}^+/\text{NNH}^+$.

Finally, high energy level calculations for $\text{HNN}^+/\text{NNH}^+$, $\text{HCO}^+/\text{COH}^+$, HCN/CNH , and DCN/CND , were done to test the ap-

plicability, at high energy levels, of the "Particle in a Box" approximation. 1

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Chapter I

INTRODUCTION

Several triatomic molecules exhibit large amplitude bending motions. In particular hydrogen cyanide (HCN) can perform complete internal "rotation" - or bending - and thus isomerize from HCN to CNH. Clearly the traditional approach of separating the vibration-rotation Hamiltonian into a small amplitude vibrational part and a rigid rotor part is completely inappropriate for calculating the vibration rotation energy levels of such a system when the isomerization is to be taken into account.

This thesis describes the application of the semirigid bender model of Bunker and Howe [1980] to the problem of the HCN isomerization. This work involved the writing of a large (over 4500 lines of FORTRAN) computer program which, when given values for certain physical quantities of a molecule, uses the semirigid bender model to calculate the vibrational energy levels. In addition, the program is written so as to allow the least squares fitting of the model to observed transition frequencies in the spectrum of a molecule.

1.1 MODEL

Traditionally the vibration-rotation problem for polyatomic molecules has been treated by separating the vibration-rotation Hamiltonian in zeroth order into vibrational and rotational parts (see, for example, the book by Papoušek and Aliev [1982]). This separation is achieved by assuming that the vibrational displacements are infinitesimal. By using perturbation theory techniques it is possible to account for the effects of non-infinitesimal vibrational displacements on the moments of inertia and hence on the rotational structure of a molecule. This treatment has been found to work well for molecules which undergo small vibrational displacements and can, in principle, be carried out to any desired order of perturbation theory.

To consider total internal rotation, however, it is clearly inappropriate to use a model based on a zeroth order Hamiltonian which assumes infinitesimal displacements. Instead we turn to the semirigid bender Hamiltonian, first developed by Bunker and Landsberg [1977], and later extended by Bunker and Howe [1980] for the case of internal rotation.

(Bunker [1983] has written what might be called a "primer" on the various large amplitude motion models and their uses. A careful and detailed review of the bender models, including a development of the sophisticated non-rigid bender model, is given by Jensen [1983a]. A complete presentation of the development of the semirigid bender Hamiltonian will therefore not be given here.)

The semirigid bender model is a natural extension of the rigid bender model of Hougen, Bunker, and Johns [1970] (hereinafter often called HBJ). The bender models are derived by referring vibrational displacements to a flexible "reference configuration" rather than to the static equilibrium configuration as is done in the traditional approach. In these models the reference configuration is allowed to "bend with" the molecule. This is done by introducing a coordinate to describe the bending motion as is shown in Fig. 1 where either of the angles ρ or τ may be used as the bending coordinate. As the molecule bends, the bending coordinate thus varies from 0, at the linear HCN configuration, all the way around to π at the linear CNH configuration. In this figure "a" is the centre of mass of the CN moiety. The reference configuration is thus specified by the bending angle and the bond lengths r_{Ha} and r_{CN} . The relative orientation of the reference configuration and the molecule fixed axes is specified by the angle ϵ as shown in Fig. 2. The dependence of ϵ on the bending angle can be chosen so as to simplify or remove terms in the semirigid bender Hamiltonian.

In the rigid bender model the bond lengths of the reference configuration are fixed at their equilibrium values. Allowing the reference configuration bond lengths to vary with the bending angle enables the reference configuration to follow the bottom of the potential valley as the molecule bends, thus giving rise to the semirigid bender model (Bunk-

er and Landsberg [1977]) which is well able to model such very large amplitude motions as complete internal rotation.

The semirigid bender Hamiltonian is derived by the same arguments as were used by HBG to obtain the rigid bender Hamiltonian (and *not* by merely substituting variable reference configuration bond lengths into the final expressions obtained for the rigid bender Hamiltonian - which seems to be implied by the text of Bunker and Landsberg [1977]). The semirigid bender Hamiltonian H_{rb} that is obtained is part of the total vibration rotation Hamiltonian $H_{vr} = H_{rbs}$ (rbs = rotation-bending-stretching) which is given for arbitrary choice of the angle ϵ by,

$$H_{vr} = H_{rb} + H_s \quad (1)$$

$$= H_b + H^{(z)} + H^{(xy)} + H^{(x\rho)} + H_s,$$

where,

$$\begin{aligned} H_b = & \frac{1}{2} \mu_{\rho\rho} J_\rho^2 + \frac{1}{2} [J_\rho, \mu_{\rho\rho}] J_\rho \\ & + \frac{1}{2} \mu^{1/2} [J_\rho, \mu_{\rho\rho} \mu^{1/2} [J_\rho, \mu^{1/2}]] \\ & + V_0(\rho), \end{aligned}$$

$$H^{(z)} = \frac{1}{2} \mu_{zz} J_z^2,$$

$$\begin{aligned} H^{(xy)} = & \frac{1}{2} \mu_{xx} J_x^2 + \frac{1}{2} \mu_{yy} J_y^2 \\ & + \frac{1}{2} \mu_{yz} (J_y J_z + J_z J_y), \end{aligned}$$

$$H^{(x\rho)} = \frac{1}{2} [J_\rho, \mu_{x\rho}] J_x + \frac{1}{2} \mu_{x\rho} (J_x J_\rho + J_\rho J_x),$$

$$H_s = \text{a Hamiltonian for the stretching vibrations,}$$

where,

$$J_\rho = -i \hbar \partial / \partial \rho,$$

J_x, J_y, J_z = the molecule fixed components of the angular momentum operator,

$\mu_{\alpha\beta}$ = the $\alpha\beta$ ($\alpha, \beta = x, y, z, \rho$) element of the inverse of the extended moment of inertia tensor $I_{\alpha\beta}$ (see Appendix A),

$$\mu = |\mu_{\alpha\beta}| = \det(\mu_{\alpha\beta}),$$

$V_0(\rho)$ = the true bending potential function.

The elements of the $\mu_{\alpha\beta}$ tensor are all evaluated as analytic functions of the bending angle (see Appendix A) but their variation with respect to the stretching coordinates

has been ignored. This approximation is reasonable in this treatment as the stretching coordinates are now truly "small amplitude" coordinates for even large amplitude bending motions. In principle all of the μ 's should have superscript zeros to indicate this approximation, but in the interest of simplicity these superscripts have been omitted.

The true bending potential function $V_b(\rho)$ is the potential energy evaluated along the minimum of the potential energy valley as the molecule bends from $\rho=0$ to $\rho=\pi$. From the Born-Oppenheimer separation, this energy is the electronic eigenvalue as the nuclear configuration follows the potential valley and is that which could be obtained directly in an *ab initio* calculation.

In the semirigid bender model the bond lengths are taken as functions of the bending angle τ . The vibration-rotation (or stretching-bending-rotating) Schrödinger equation resulting from this Hamiltonian may be separated parametrically in τ by writing the wavefunctions as products,

$$\psi_{vr} = \psi_{rbs}(\tau) = \psi_{rb}(\tau) \psi_s^\tau, \quad (2)$$

where ψ_s^τ is an eigenfunction of the stretching Hamiltonian evaluated at τ , which we denote H_s^τ ,

$$H_s^\tau \psi_s^\tau = E_s^\tau \psi_s^\tau. \quad (3)$$

Each ψ_s^τ is a function of the two stretching normal coordinates, Q_1 and Q_2 , i.e.

$$\psi_s^\tau = \psi_s^\tau(Q_1, Q_2),$$

(4)

where it must be remembered that the stretching normal coordinates are separately defined at each angle τ of the reference configuration.

Substitution of the product wavefunction into the vibration-rotation Schrödinger equation gives,

$$E_{rb} \psi_{rb} = (H_{rb}(\tau) + E_s^\tau) \psi_{rb},$$

(5)

where E_s^τ is a function of τ and appears as a potential energy term, exactly analogous to the appearance of the electronic eigenvalue as a potential energy term in the vibrational Hamiltonian following the parametric Born-Oppenheimer separation of the complete molecular Hamiltonian. We write E_s^τ as the standard anharmonic series,

$$E_s^\tau = G^\tau(v_1, v_2) \\ = \sum_r \omega_r^\tau (v_r + \frac{1}{2}) + \sum_{rs} x_{rs}^\tau (v_r + \frac{1}{2}) (v_s + \frac{1}{2}),$$

where,

$$r, s = 1, \text{ or } 3,$$

(6)

where the ω_r^τ are the harmonic stretching frequencies and the x_{rs} are the anharmonicity factors, and where both the $\omega_r(\tau)$ and the $x_{rs}(\tau)$ depend on the bond angle τ . Note that E_s^τ depends on the stretching vibration quantum numbers (v_1, v_3) .

This equation is solved using the method of Bunker and Stone [1972] (hereinafter sometimes called BS) which first requires the grouping of the terms of the Hamiltonian as,

$$\begin{aligned} H &= [H_D + H^{(z)} + E_s^\tau] + [H^{(xy)} + H^{(xp)}] \\ &= H_0 + H_I, \end{aligned} \quad (7)$$

where H_0 thus describes the bending and axial rotation, while H_I describes the "end-over-end" rotation. The potential energy term that appears in H_0 consists of the true bending potential function V_0 plus the stretching vibration eigenvalue E_s^τ , and is the "effective potential" V_{eff} ,

$$\begin{aligned} V_{\text{eff}}(\tau) &= V_0(\tau) + E_s^\tau \\ &= V_0(\tau) + G^\tau(v_1, v_3). \end{aligned} \quad (8)$$

V_{eff} is thus different for each stretching (or "small amplitude") state (v_1, v_3) and is the potential function that the molecule sees as it bends in a particular (v_1, v_3) stretching state. The procedure is to obtain numerically a sequence of bending eigensolutions of H_0 for each stretching state

(v_1, v_2) by a process described below. The resulting wavefunctions are then multiplied by a basis set for H_I and the total Hamiltonian $H = H_0 + H_I$ is numerically diagonalized in terms of the product basis set to give the bending-rotation energy levels for the small amplitude state in question.

In the present work this second step - that is the diagonalization of the full Hamiltonian - will *not* be considered. The main goal of Chapters II and III of this thesis is to study the bending potential function of HCN/CNH in the $\tilde{X}$ 'A' ground and $\tilde{A}$ 'A' first excited electronic states. To do this it is sufficient to consider pure vibrational levels without rotation. In chapter IV the intensities of various vibrational transitions are calculated. Although some of these transitions involve states with rotation, sample calculations that were done showed that the actual mixing of the eigenfunctions of H_0 by H_I is very small. This slight mixing has an insignificant effect on the intensity of a complete vibrational transition. It is therefore sufficient for the present work to consider only the Schrödinger equation involving H_0 .

One point of technical importance is that in the calculations described below (notably the calculation of absorption intensities for CNH) the angle ϵ , which specifies the orientation of the molecular fixed axes with respect to the reference configuration (see Fig. 2), had to be chosen differently than was done in HBJ and subsequent works. For the

present calculations ϵ was set equal to zero with the result that the molecular fixed axes remained parallel to the CN moiety of the reference configuration. On H_0 , this only has the effect of changing the expressions for the elements of the μ tensor from the forms they have in BS. These tensor elements may be found in Appendix A. H_I is changed by the addition of the extra term $H^{(XP)}$ (as can be seen by comparison with Eq. 36 of HBJ or Eq. 8c of BS).

The goal, then, is to determine the eigenvalues of H_0 , i.e. to solve,

$$H_0 \cdot \Psi_0 = E_0 \cdot \Psi_0,$$

(9)

where,

$$\begin{aligned} H_0 = & \frac{1}{2} \mu_{\rho\rho} J_{\rho}^2 + \frac{1}{2} [J_{\rho}, \mu_{\rho\rho}] J_{\rho} \\ & + \frac{1}{2} \mu^{1,1} [J_{\rho}, \mu_{\rho\rho} \mu^{-1,1} [J_{\rho}, \mu^{1,1}]] \\ & + \frac{1}{2} \mu_{zz} J_z^2 \\ & + V_{\text{eff}}. \end{aligned}$$

To do this Ψ_0 is written as a product of a wavefunction for rotation about the molecule-fixed z-axis ψ_{rot}^K , that is an eigenfunction of $H^{(Z)}$,

$$\psi_{\text{rot}}^K(\chi) = \frac{1}{\sqrt{2\pi}} e^{iK\chi},$$

(10)

$$H^{(Z)} \psi_{\text{rot}}^K = -K^2 \hbar^2 \mu_{zz} \psi_{\text{rot}}^K,$$

(where χ is the third of the Euler angles θ, ϕ, χ , which specify the orientation of the molecule fixed axes x, y, z with respect to the space fixed axes X, Y, Z , and thus describes rotation about the molecule fixed z -axis), and a bending eigenfunction (which is not known at this point) which is written,

$$\psi_b^K(\rho) = [\mu_{\rho\rho}]^{-1/2} \phi_K(\rho), \quad (11)$$

so as to remove a linear derivative term in the Schrödinger equation. Substituting the product function,

$$\Psi_0 = \psi_b^K(\rho) \psi_{\text{rot}}^K(\chi), \quad (12)$$

into the Schrödinger equation and integrating with respect to χ after left multiplying by $(\psi_{\text{rot}}^K)^*$ gives the equation for the auxiliary bending wavefunction (Eqs. 12 and 13 of BS),

$$\begin{aligned} (\partial^2/\partial\rho^2) \phi_K(\rho) = [f_1(\rho) + K^2 f_2(\rho) \\ + \frac{2}{h^2 \mu_{\rho\rho}} (V_{\text{eff}}(\rho) - E_0)] \phi_K(\rho), \end{aligned} \quad (13)$$

where,

$$\begin{aligned} f_1(\rho) &= \mu^{1/4} [\mu_{\rho\rho}]^{-1/2} (\partial^2/\partial\rho^2) (\mu^{-1/4} \mu_{\rho\rho}^{1/2}), \\ f_2(\rho) &= \mu_{zz}/\mu_{\rho\rho}. \end{aligned}$$

As a part of this work a "compacted" analytic expression for $f_1(\rho)$ was obtained. This was the first time that this had been done for a semirigid bender model. In semirigid bender calculations $f_1(\rho)$ had previously always been determined numerically using the expression given above. As $f_1(\rho)$ is singular at $\rho = 0$ and $\rho = \pi$ this numerical procedure required a separate calculation on a much finer grid than was used for the numerical integration. Since this work an analytic expression for $f_1(\rho)$ for a 4-atomic semirigid bender model has been developed by Jensen [1983b]. Jensen's expression, however, is not in a "compacted" form but requires computer summation over the coordinates of each atom in the molecule.

Eq. 13 for the auxiliary bending wavefunction ϕ_K is solved for each small-amplitude stretching and K-rotational state (v_1, v_2) by using the technique of Numerov-Cooley numerical integration (Cooley [1961]) to obtain a series of bending wavefunctions and energies. The application of this technique to the specific case of a double minimum potential function is described by Bunker and Howe [1980]. In the present work a slight rearrangement of the Numerov-Cooley method was found to give a somewhat simpler version of the technique which does not require the introduction of the "y" variables. This revised procedure is outlined in Appendix B.

In all of the work reported here, 2000 points were used in the numerical integration of the bender equation. The first thirty points at the start ($\rho = 0$) and finish ($\rho = \pi$) of the integrations were done using the series solution technique so as to deal with the singularities at these points. This is described in more detail by Bunker^{and} Landsberg [1977] and Jensen [1983a].

The computer program written to do this numerical integration allows the least squares fitting of the various physical quantities of the model to observed vibrational energies and spectral transition frequencies. To do this the dependance on τ of the quantities appearing in the model had to be expressed in some functional form. As in Bunker and Howe [1980] this was done by using a power series expansion in $(1 - \cos \tau)$,

$$F(\tau) = \sum_{n=0}^{n_{\max}} F^{(n)} (1 - \cos \tau)^n.$$

(14)

where $F(\tau)$ represents each of the eight physical quantities which appear in the model,

$$\begin{aligned}
 & r_{\text{Ha}}(\tau), \\
 & r_{\text{CN}}(\tau), \\
 & V_0(\tau), \\
 & \omega_r(\tau), \quad r = 1, \text{ or } 3, \\
 & x_{rs}(\tau), \quad r, s = 1, \text{ or } 3.
 \end{aligned}$$

(15)

The expansion in $(1 - \cos \tau)$ is suitable in this problem as the first derivative with respect to τ , of this series, vanishes at both $\tau = 0$ and $\tau = \pi$. Thus the various quantities are ensured of smoothly reaching a limit at the linear configurations.

In practice it turns out that the coefficients of these power series are often enormously large. For example several of the coefficients of the power series for the potential function of the A 'A' first excited electronic state of HCN/CNH were of the order of $2,000,000 \text{ cm}^{-1}$, or more than 100 times larger than the total range in height of the potential function itself! The actual form of the potential function results from a large measure of cancelling of the terms in the power series. Due to this it is probably not possible, and it certainly would not be trivial, to do a least squares fitting directly of the power series coefficients. In fact it is not desirable to do such a fitting. What is more appropriate is to introduce as parameters vari-

ous physical properties of the quantities in question. For example the potential function is described in terms of barrier heights, energy differences between potential minima, and so on. It is in terms of such *physically significant* parameters that the least squares fittings described in this work were done.

The actual set of parameters chosen for a particular problem depends on the experimental data available for a least squares fitting, the available *ab initio* calculations, and, in a more fundamental way, on the geometry of the state being considered. In each problem considered in this work a separate choice of parameters was made. These choices are described in detail in the relevant chapters.

One complication created by choosing such parameters is that the relationship between them and the set of power series coefficients actually used in the model, is rather complicated. This relationship is expressed in terms of a set of coupled linear and nonlinear equations which must be solved in order to relate the input parameters and the actual power series coefficients. In particular, several of these relationships involve the conversion between the two bending angles ρ and τ .

It will be noted that both ρ and τ have been used as the bending coordinate. ρ was used for the variable of integration and in the Schrödinger equation as use could then be made of many algebraic results available from earlier work.

τ , however, was used in the series expansions for the various quantities of the model. This use of both bending angles required the conversion between ρ and τ , and also between various first and higher order derivatives in terms of these variables. This was straightforward and was done by making use of the geometric identity, derivable from Fig. 1,

$$r_{\text{Ha}}(\tau) \sin(\rho - \tau) = \frac{m_{\text{N}}}{m_{\text{C}} + m_{\text{N}}} r_{\text{CN}}(\tau) \sin \rho, \quad (16)$$

which was solved numerically using the Newton-Raphson method. The interconversion of the various derivatives was done by repeated implicit differentiation of this identity to obtain $\partial\tau/\partial\rho$, $\partial^2\tau/\partial\rho^2$, etc. as required.

In summary, Eq. 9 is solved for the bending and K-type rotational energy levels and wavefunctions of an internally rotating ABC molecule. Writing the eigenfunctions in the separated form of Eq. 12 (see Eqs. 10 and 11) leads to a one dimensional partial differential equation (Eq. 13) which can be solved numerically for the energies E , and wavefunctions $\phi_K(\rho)$. The solution of this equation is discussed in Chapter II for the $\tilde{X}$ 'A' ground state of HCN/CNH, in Chapter III for the $\tilde{A}$ 'A' first excited electronic state of HCN/CNH, and in Chapter V for the ground electronic states of $\text{HCO}^+/\text{COH}^+$ and $\text{HNN}^+/\text{NNH}^+$. The use of the resulting wavefunctions for the calculation of transition intensities for the vibrational bands of the $\tilde{A}-\tilde{X}$ electronic transition of HCN/CNH is described in Chapter IV.

Chapter II

THE $\tilde{X}$ 'A' GROUND ELECTRONIC STATE OF HCN/CNH

The vibrational levels of the $\tilde{X}$ 'A' ground electronic state of HCN/CNH have been the object of much experimental research (see in particular the references cited in Tables I, II, III, IV, and VI, given in Table 11, and which are located in Section 2.2). It is known that both the HCN and CNH isomers are linear in their ground electronic state.

The possibility that HCN may perform internal isomerization to CNH has prompted the *ab initio* calculation of the complete HCN/CNH bending potential function by Pearson, Schaefer, and Wahlgren [1975]. In this calculation they determined that the CNH potential minimum lies about 5000 cm^{-1} above that of HCN, and is separated from HCN by a potential barrier of about 17000 cm^{-1} . CNH has been seen in hot HCN using microwave absorption by Blackmann *et. al.* [1976], and in infrared absorption by Maki and Sams [1981]. These observations confirm that internal isomerization does indeed occur in HCN.

This chapter describes the fitting of the semirigid bend-der model to the observed vibrational levels of HCN/CNH in order to empirically determine the bending potential function.

In this work the vibrational levels of the $\tilde{X}$ 'A' ground state of HCN/CNH are labelled according to the modern convention (Herzberg [1966]), (v_1, v_2, ℓ, v_3) , where v_1 is the quantum number for the "H" stretching vibration (C-H stretch for HCN, and N-H stretch for CNH), v_2 is the *linear convention* bending quantum number, and v_3 is the quantum number for the C-N stretching vibration. ℓ is the vibrational angular momentum quantum number.

2.1 PARAMETERIZATION

HCN and CNH are both linear in their ground electronic states. In the parameterization of the physical quantities that occur in the model (Eq. 15) it is thus reasonable to introduce parameters that specify the properties of these quantities at the two linear configurations, $\rho = 0$ (HCN), and $\rho = \pi$ (CNH). The true bending potential function V_ρ requires a more detailed parameterization which is described below.

2.1.1 Bond Lengths

The C-N and H-a bond length functions are each parameterized by four parameters. The first of these parameters are the values of the bond lengths at the linear equilibrium geometries of each isomer,

$$\begin{aligned}
 r_{\text{Ha}}(\text{HCN}) &= r_{\text{Ha}}(\tau = 0), & r_{\text{Ha}}(\text{CNH}) &= r_{\text{Ha}}(\tau = \pi), \\
 r_{\text{CN}}(\text{HCN}) &= r_{\text{CN}}(\tau = 0), & r_{\text{CN}}(\text{CNH}) &= r_{\text{CN}}(\tau = \pi).
 \end{aligned}
 \tag{17}$$

The second derivatives, with respect to τ , of these bond lengths at each linear configuration are used as the remaining four bond length parameters,

$$\begin{aligned}
 r''_{\text{Ha}}(\text{HCN}) &= r''_{\text{Ha}}(\tau = 0), & r''_{\text{Ha}}(\text{CNH}) &= r''_{\text{Ha}}(\tau = \pi), \\
 r''_{\text{CN}}(\text{HCN}) &= r''_{\text{CN}}(\tau = 0), & r''_{\text{CN}}(\text{CNH}) &= r''_{\text{CN}}(\tau = \pi).
 \end{aligned}
 \tag{18}$$

As the bond lengths specify the geometry of the molecule, and hence its rotational constants, they cannot reasonably be determined in a least squares fitting involving only vibrational data. Instead these parameters were held fixed in the least squares fitting at values chosen so that the bond length functions modelled the *ab initio* values of Pearson, Schaefer, and Wahlgren [1975]. This was done by fixing the bond length functions at linearity directly to the *ab initio* values. The four other bond length parameters, corresponding to the second derivatives of the bond lengths, were determined in a least squares fitting of the bond length functions to all of the *ab initio* points. The bond length constants thus determined, and used in the study of the ground state, are presented in Table 1. The bond length functions generated by these constants are shown in Fig. 3.

TABLE 1

HCN/CNH Ground State Bond Length
Parameters.

as Fixed for Use in the Least
Squares Fitting of HCN/CNH.

Parameter	HCN	CNH
$r_{\text{Ha}} / \text{\AA}$	1.685	1.536
$r_{\text{CN}} / \text{\AA}$	1.150	1.169
$r''_{\text{Ha}} / \text{\AA rad}^{-2}$	-0.970	-0.891
$r''_{\text{CN}} / \text{\AA rad}^{-2}$	0.050	0.079

2.1.2 Potential Function

Five parameters were used to specify the bending potential function for the $\tilde{X}$ 'A' ground state of HCN/CNH. These parameters are indicated on the schematic potential-function shown in Fig. 4. H_0 and τ_0 specify the height and bending angle of the barrier to internal rotation. ΔE is the CNH-HCN equilibrium energy difference while $f_{\alpha\alpha}(\text{HCN})$ and $f_{\alpha\alpha}(\text{CNH})$ are the harmonic bending force constants of HCN and CNH. These last two parameters are defined as,

$$\begin{aligned} f_x &= \left(\partial^2 / \partial \alpha_x^2 V(\tau) \right) \Big|_{\tau_x} \\ &= \left(\partial^2 / \partial \tau^2 V(\tau) \right) \left(\partial \tau / \partial \alpha_x \right)^2 \Big|_{\tau_x} \\ &\quad + \left(\partial / \partial \tau V(\tau) \right) \left(\partial^2 \tau / \partial \alpha_x^2 \right) \Big|_{\tau_x}, \end{aligned} \quad (19)$$

where α_x , $x = \text{HCN or CNH}$, is the bond angle coordinate corresponding to HCN or CNH as illustrated in Fig. 5. The derivatives in this expression are evaluated at the HCN and CNH equilibrium configurations. The second term vanishes as, by definition, $\partial / \partial \tau V(\tau) \Big|_{\tau_{\text{equi}}} = 0$. The factor corresponding to the second derivative of the potential function with respect to τ is determined from the power series expansion. For HCN the derivative of τ with respect to α_{HCN} is determined by noting that $\alpha_{\text{HCN}} = \pi - \rho$ and solving for $\partial \tau / \partial \rho$ after implicitly differentiating the geometric identity relating τ and ρ which was presented above (Eq. 16),

$$r_{\text{Ha}}(\tau) \sin(\rho - \tau) = \frac{m_{\text{N}}}{m_{\text{C}} + m_{\text{N}}} r_{\text{CN}}(\tau) \sin \rho, \quad (20)$$

For CNH a similar geometric identity relating τ and α_{CNH} can be easily derived,

$$r_{\text{Ha}}(\tau) \sin(\tau - \alpha) = \frac{m_{\text{C}}}{m_{\text{C}} + m_{\text{N}}} r_{\text{CN}}(\tau) \sin \alpha, \quad (21)$$

and used in the same fashion.

2.1.3 Stretching Frequencies

In the study of the $\tilde{X}$ 'A' ground state of HCN/CNH it proved to be possible to determine the dependance on bending angle of the harmonic stretching frequencies, $\omega_1(\tau)$, and $\omega_3(\tau)$. As a result, the bending potential function V_0 that is obtained in the least squares fitting is corrected for the effects of stretching vibration averaging - i.e. in this case it is corrected for the variation with bending angle of the zero-point energy of the stretching vibrations - and is thus the true bending potential function V_0 which can be directly compared to the *ab initio* potential function.

Due to the limited data available for CNH, the harmonic stretching frequencies $\omega_r(\tau)$ were parameterized with only three parameters: their values at both the HCN and CNH configurations $\omega_r(\text{HCN})$, $\omega_r(\text{CNH})$, $r=1,3$, and their second derivatives with respect to τ , evaluated at the HCN configuration, $\partial^2 \omega_r(\tau) / \partial \tau^2 |_{\tau=0} = \omega_r''(\text{HCN})$; $r=1,3$.

It was not possible to determine the dependence on the bending angle of the anharmonic functions $x_{rs}(\tau)$, $r,s=1,3$, which were therefore used as constant functions of the bending angle, $x_{rs}(\tau) = x_{rs}(0)$.

2.2 DATA AND RESULTS

All extant vibrational data for the $\tilde{X}$ 'A' ground states of HCN and CNH were used in a detailed study of the HCN/CNH isomerization. The data used in this study and the results obtained are discussed in detail in the paper of Ross and Bunker [1983] which is enclosed here.

The Potential Function for HCN/CNH Isomerization

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The semirigid bender model (P. R. Bunker and D. J. Howe, *J. Mol. Spectrosc.* 83, 288-303 (1980)) has been developed to fit the observed vibrational energy levels of the ground electronic state of HCN/CNH and DCN/CND allowing for the complete bending (internal rotation) of HCN into CNH and of DCN into CND. From the fit we have been able to determine the bending potential function and the contribution to the bending potential that arises from the effect of averaging over the two stretching vibrations. The results are compared with ab initio calculations.

I. INTRODUCTION

The isomerization of HCN to CNH, observed to occur in hot HCN (1, 2), is probably the result of large amplitude internal bending. The bending energy levels of HCN/CNH, treated as one molecule, were calculated by Bunker and Howe (3) using the semirigid bender Hamiltonian for a triatomic molecule (4), together with an ab initio geometry and potential surface (5). In the present paper we extend the model by allowing for the effects of stretching vibration averaging on the bending potential function and we adjust the potential to fit the experimental vibrational data available for HCN/CNH and DCN/CND. As a result we have been able to determine from experiment the contribution of the stretching vibration averaging to the effective bending potential, and have thereby obtained the true bending potential. These results can be compared to ab initio results (5, 6).

II. THE HAMILTONIAN

The semirigid bender Hamiltonian for the rotation-bending motion of a triatomic molecule was introduced by Bunker and Landsberg (4), and is a development of earlier work on triatomic molecules (7, 8). In this Hamiltonian the molecule is described as rotating and bending with bond lengths that change with bond angle in order to follow the valley in the potential function as the molecule bends. The molecular coordinates are defined in Fig. 1, where "a" is the center of mass of the CN moiety and we can use either ρ or τ as the bending coordinate. The semirigid bender is an improvement over the earlier rigid bender (8), in which the bond lengths are held fixed, and this improvement is particularly necessary for the description of the bending isomerization of the HCN/CNH system. In the present work we concentrate only on the vibrational energy levels and we can write the Hamiltonian as (see Eq. (2a) of (3))

Figure 6: Fig. 1 The Parameters of the Reference Configuration.

FIG. 1. The parameters specifying the reference configuration. The center of mass of the CN moiety is denoted "a" and the angular configuration is specified by either ρ or τ .

$$H_b = \frac{1}{2} \mu_{pp} J_p^2 + \frac{1}{2} [J_p, \mu_{pp}] J_p + \frac{1}{2} \mu^{1/4} [J_p, \mu_{pp} \mu^{-1/2} [J_p, \mu^{1/4}]] + V_{\text{eff}}(\rho) \quad (1)$$

where $J_p = -i\hbar \partial/\partial \rho$, $\mu_{pp} = 1/I_{pp}$ with I_{pp} (which involves r_{CN} and r_{Ha}) given as in Eq. (14d) of Sarka (9), and we use

$$V_{\text{eff}}(\rho) = V_0(\rho) + \sum_r \left(v_r + \frac{1}{2} \right) \omega_r(\rho) + \sum_{r,s} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right) x_{rs}(\rho) \quad (2)$$

where $r, s = 1$ or 3 , for the effective bending potential function. The true bending potential function is $V_0(\rho)$. Allowance for the variation of the stretching vibration energies with bending angle gives rise to V_{eff} (see Eq. (A4) of Ref. (10) and Eq. (20) of Ref. (11)), as opposed to V_0 , in Eq. (1).

The Hamiltonian involves the eight factors r_{CN} , r_{Ha} , V_0 , ω_1 , ω_3 , x_{11} , x_{33} , and x_{13} , all of which depend on the bending angle (ρ or τ). We expand each of these functions as a power series in $(1 - \cos \tau)$, i.e., we write

$$F = \sum_{n=0}^{n_{\text{max}}} F^{(n)} (1 - \cos \tau)^n \quad (3)$$

where F is one of the eight functions and the expansion parameters $F^{(n)}$ remain to be determined. Rather than optimizing the values of the $F^{(n)}$, by fitting the eigenvalues of H_b to experimental data, it is more appropriate to optimize linear combinations of the $F^{(n)}$ corresponding to physically interpretable parameters. Hence the parameters we adjust in the fitting are as described below.

(a) For the bond lengths the following parameters:

$$r_{CN}, r_{Ha},$$

$$r'_{CN} = (\partial^2 r_{CN} / \partial \tau^2), \text{ and } r'_{Ha},$$

each for $\tau = 0$ (i.e., HCN) and $\tau = \pi$ (i.e., CNH), to give

8 bond length parameters in all.

(b) For the stretching vibrations the following 15 parameters:

$$\omega_1(\text{HCN}) = \omega_1(\tau = 0),$$

$$\omega_1(\text{CNH}), \quad \omega_3(\text{HCN}), \quad \omega_3(\text{CNH}),$$

$$\omega'_1(\text{HCN}) = (\partial^2 \omega_1 / \partial \tau^2)_{\tau=0},$$

$$\omega_3^s(\text{HCN}),$$

$$x_{r_3}(\text{HCN}), \quad x_{r_3}(\text{CNH}), \quad \text{and} \quad x_{r_3}^s(\text{HCN}).$$

(c) For the bending potential the following 5 parameters:

$f_{\alpha\alpha}(\text{HCN})$, the HCN bending force constants,

$f_{\alpha\alpha}(\text{CNH})$, the CNH bending force constant,

H , the height of the barrier to isomerization measured
from the HCN potential minimum,

τ_0 , the bending angle at which the barrier occurs, and

ΔE , the height of the CNH minimum above the HCN minimum.

There are thus a maximum of 28 parameters that we can try to determine by fitting to the data.

The bond length functions should in principle depend on the values of v_1 and v_3 , but we have not allowed for that; this would clearly be of more importance in the calculation of rotational energies which we do not consider here. The stretching vibration parameters $\omega_1^s(\text{CNH})$, $\omega_3^s(\text{CNH})$, and $x_{r_3}^s(\text{CNH})$ have not been included because of the limited data available for the CNH molecule.

With assumed values for the parameters we solve the bending eigenvalue equation

$$H_b \Psi_b(\rho) = E_b \Psi_b(\rho) \quad (4)$$

using the Numerov-Cooley integration technique, as described in (3). We use ρ rather than τ as the variable of integration in order to make immediate use of the results in Ref. (7). To obtain τ for each value of ρ we must solve

$$r_{\text{Ha}}(\tau) \sin(\rho - \tau) = \frac{m_{\text{N}}}{m_{\text{C}} + m_{\text{N}}} r_{\text{CN}}(\tau) \sin \rho, \quad (5)$$

where m_{C} and m_{N} are the atomic masses of carbon and nitrogen. By repeated differentiation of Eq. (5) we are able to obtain the derivatives $\partial\tau/\partial\rho$, $\partial^2\tau/\partial\rho^2$, etc. needed in the evaluations. We have obtained $f_1(\rho)$ (see Eq. (43) of Ref. (7) and Eq. (12) of Ref. (4)) analytically rather than numerically as was done in (3) and (4).

The computer program that we have written to solve Eq. (4) allows us to do a direct least squares fit to experimental data in order to obtain the optimum values of the parameters. In particular we can determine the true bending potential $V_0(\rho)$ and the effective potential $V_{\text{eff}}(\rho)$ for each (v_1, v_3) stretching state.

III. THE DATA

Many experimental vibrational band origins for HCN/CNH and DCN/CND are available, and they involve a significant number of vibrational states. Wherever reasonably possible we have reduced these band origins to vibrational energies referred to the $(0, 0^0, 0)$ ground state of HCN or CNH as appropriate. With the exception of

the low resolution fluorescence data of Baronavski (12) all the data are given unit weight which we have chosen to correspond to the estimated precision of the model (of the order of 1 cm^{-1}).

(a) *The HCN Data*

A large amount of infrared spectroscopic data is available for HCN. We have combined the best available infrared band origins to obtain the vibrational energies, referred to the $(0, 0^0, 0)$ level, of the observed states having $l = 0$. These values are reported in the "obs" column of Table I. To obtain the energies from the published band origins for hot bands involving $(0, 1^1, 0)$ we have used the values $(13, 14)$ 713.460 cm^{-1} for $\nu_0(0, 1^1, 0)$ and 1.4818 cm^{-1} for $B(0, 1^1, 0)$ to correct, where necessary, the published hot band origins. All other hot bands having $l' = 0$ involve $l'' = 0$ states only and for these the lower state energies were taken from the "obs" column of Table I.

Lehmann *et al.* (24) have recently observed several highly excited stretching states of HCN in direct absorption from the $(0, 0^0, 0)$ vibrational ground state using an intracavity photoacoustic technique, and the vibrational energies that they obtain are included with the infrared data in Table I.

Baronavski (12) has observed laser induced fluorescence from the $\tilde{A}$ excited electronic state of HCN to many highly excited vibrational levels of the ground electronic state. In particular the ground state levels observed in fluorescence from $\tilde{A}(0, 1, 0)^{K=1}$ are of the type $(0, \nu_2^0, \nu_3)$ which, not involving rotation, may be fitted with our model. We obtain the ground state vibrational energies by subtracting the fluorescence frequencies from the electronic band origin determined in the ultraviolet absorption work of Herzberg and Innes (27): $\nu_0[\tilde{A}(0, 1, 0)^1 - \tilde{X}(0, 0^0, 0)] = 53\,218 \text{ cm}^{-1}$. The ground state energies thus calculated are presented in the "obs" column of Table II. Because the fluorescence spectrum is weak, often overlapped, and of moderate resolution, these energies are rather imprecise. We obtain an estimate of their precision by comparing, in Table III, those values which are also known from infrared work. It is clear from this comparison that the uncertainty of the fluorescence derived vibrational energies is about 100 cm^{-1} . Accordingly these values were given a weight of 10^{-4} in the least squares fitting.

(b) *The CNH Data*

Three excited vibrational levels having $l = 0$ have been observed in the high resolution infrared work of Maki and Sams (2) and Winter and Jones (28). As two of these levels are seen in hot bands, for which the ground state energies are only imprecisely known, we use the two transition frequencies directly in the least squares fitting. The ν_3 C-N stretching frequency has only been observed in an Ar matrix (29).

To estimate the $2\nu_2^0$ energy of CNH we use the Ar matrix value (29) of 477 cm^{-1} for ν_2^0 and assume the same relative matrix shift as for HCN to get the estimate of 470.7 cm^{-1} for the gas phase value. Estimating $2\nu_2^1 = 2(\nu_2^0)$, and taking $2\nu_2^0 = 2\nu_2^1 - 9.4 \text{ cm}^{-1}$ from (2) we obtain $2\nu_2^0 = 932 \text{ cm}^{-1}$ for gas phase CNH; this is reported with the other CNH energies in the "obs" column of Table IV.

TABLE 2

Table I HCN Vibrational Energies: IR Derived Values, Observed and Calculated.

TABLE I

The Observed HCN Vibrational Energies (in cm^{-1}) Derived from Infrared Spectroscopic Results

Stretching State (ν_1, ν_3)	Bending State ν_2	obs	obs-calc ^a	Ref.
(0,0)	0*	0	-	
	2*	1411	3	(13), (14) ^b
	4*	2803	4	(15)
(0,1)	0*	2097	-2	(16)
	2*	3502	1	(15) ^c , (17)
	4*	4888	2	(18)
(0,2)	0*	4173	-5	(15)
	2*	5572	-3	(18) ^d
(1,0)	0*	3311	3	(19), (20)
	2*	4684	-0	(20) ^e , (21) ^b
	4*	6037	-6	(20) ^d
(1,1)	0*	5394	4	(20) ^e
	2*	6761	1	(18) ^b
(2,0)	0*	6520	2	(20) ^f , (22)
(2,1)	0*	8586	4	(23)
	2*	9914	-3	(23)
(2,3)	0*	12658	8	(23)
(2,4)	0*	14654	-2	(23)
(2,5)	0*	16640	-1	(24)
(3,0)	0*	9627	-2	(23)
(3,1)	0*	11674	0	(24)
(3,2)	0*	13702	2	(23)
(3,3)	0*	15711	3	(24)
(4,0)	0*	12636	-5	(24)
(4,1)	0*	14670	2	(23) ^g
(4,2)	0*	16674	-2	(24)
(5,0)	0*	15552	-1	(24)
(5,1)	0*	17550	-13	(24)
(6,0)	0*	18377	10	(24)

^aThe calculated values use the HCN/CNH parameters of Tables VII, VIII, and IX.

^bCalculated from a (0,1¹,0) hot band.

^cCalculated from a (0,2⁰,0) hot band.

^dCalculated from a (0,4⁰,0) hot band.

^eCalculated from a (0,0⁰,1) hot band.

^fCalculated from a (1,0⁰,0) hot band.

(c) The DCN Data

The [data] [DCN] that we use consist mainly of vibrational energies calculated by combining band origins obtained from various published infrared absorption experiments. This was done as for HCN and we use $\nu^0(0, 1^1, 0) = 570.258 \text{ cm}^{-1}$ and $B(0, 1^1, 0) = 1.2121 \text{ cm}^{-1}$ from (13). The energy of the ν_3 vibration has been most precisely

TABLE 3

Table II HCN Vibrational Energies: UV Derived Values,
Observed and Calculated.

TABLE II

The Observed HCN Vibrational Energies from Ref. (12) (in cm^{-1})

Stretching State (ν_1, ν_3)	Bending State ν_2	obs	obs-calc ^a
(0,0)	0*	-	
	2*	-	
	4*	2662	-137
	6*	4294	123
	8*	5644	126
	10*	6965	121
	12*	8193	50
(0,1)	14*	9683	270
	0*	-	
	2*	3541	40
	4*	5002	116
	6*	6314	64
	8*	7660	67
	10*	8990	78
(0,2)	12*	10373	168
	14*	11707	237
	0*	4294	115
	2*	5644	69
	4*	6965	12
	6*	8193	-118
	8*	9683	35
(0,3)	10*	11042	81
	12*	12352	104
	14*	13677	171
	0*	6314 ^b	75
	2*	7660	31
	4*	8990	-11
(0,3)	6*	10373	20
	8*	11707 ^b	23
	10*	13041	50
	12*	14338	66
	14*	15695	171
(0,4)	0*	8193 ^b	-87
	2*	9683	19
	4*	11042	13
	6*	12352 ^b	-23
	8*	13677 ^b	-23
	10*	15021	20
	12*	16318	42
(0,5)	14*	17643	121
	0*	10373 ^b	71
	2*	11707 ^b	28
	4*	13041	2
	6*	14338 ^b	41
	8*	15695 ^b	-2
	10*	16986	-6

^aThe calculated values use the HCN/CHN parameters of Tables VII, VIII, and IX.

^bThese values result from additional assignments of blended lines in Baranavski's (12) data.

TABLE 4

Table III HCN Vibrational Energies: Comparison of IR and UV Derived Values.

TABLE III

Comparison of Ground State Vibrational Energies from Ref. (12) with Those Obtained from the Infrared Spectrum (in cm^{-1})^a

Ground State Level	Ref. (12)	Infrared ^a	Difference
(0,4 ⁰ ,0)	2662	2803	-141
(0,2 ⁰ ,1)	3541	3502	39
(0,4 ⁰ ,1)	5002	4888	114
(0,0 ⁰ ,2)	4294	4173	121
(0,2 ⁰ ,2)	5644	5572	72

^aFor infrared references see the relevant entries in Table I.

determined in the laser-Stark experiment of Freund and Maki (30), and this is reported with the infrared data for DCN in the "obs" column of Table V.

(d) The CND Data

The only excited $l = 0$ vibrational level of CND that has been observed in the gas phase is the (1, 0⁰, 0) level seen in absorption from the ground state (2). The (0, 0⁰, 1) level has been seen by Milligan and Jacobx (29) in an Ar matrix study, and we use this value uncorrected for matrix shift. The bending energy $2\nu_2^0$ is estimated as 733 cm^{-1} from the Ar matrix value of $\nu_2^0 = 374 \text{ cm}^{-1}$ (29) in the same way as we made the estimate for CNH. The CND data is given in the "obs" column of Table VI.

TABLE IV

The Experimental CNH Vibrational Energies (in cm^{-1})

Stretching State (ν_1, ν_3)	Bending State ν_2^l	obs	obs-calc ^a	Ref.
(0,0)	0 ⁺	0	-	
	2 ⁺	932 ^b	0	
(0,1)	0 ⁺	2029	0	(29)
(1,0)	0 ⁺	3653	-12	(2)
Transition				
(1,2 ⁰ ,0)-(0,2 ⁰ ,0)		3608	10	(2)
(1,0 ⁰ ,1)-(0,0 ⁰ ,1)		3650	3	(28)

^aThe calculated values use the HCN/CNH parameters of Tables VII, VIII, and IX.

^bEnergy estimated as described in Sect. III (b) of the text.

TABLE 5

Table IV CNH Vibrational Energies: Observed and Calculated.

TABLE 6

Table V DCN Vibrational Energies: Observed and Calculated.

TABLE V

The Experimental DCN Vibrational Energies (in cm^{-1})

Stretching State (ν_1, ν_2)	Bending State ν_3	obs	obs-calc ^a	Ref.
(0,0)	0*	0	-	
	2*	1130	2	(13)
(0,1)	0*	1925	1	(30)
	2*	3061	-1	(31) ^b
(0,2)	0*	3836	0	(32)
(1,0)	0*	2630	1	(31)
	2*	3729	-1	(31) ^c
(1,1)	0*	4523	0	(21)
(2,0)	0*	5220	0	(31)

^aThe calculated values use the DCN/CND parameters of Tables VII, VIII, and IX.

^bCalculated from a (0,1¹,0) band.

^cCalculated from a (0,2⁰,0) band.

IV. RESULTS

The semirigid bender model was fitted, by weighted least squares adjustment of the parameters presented in Section II, to the vibrational data presented in Section III for HCN/CNH and for DCN/CND. In the fitting of the HCN/CNH data we determined various of the stretching vibration parameters and the true bending potential function. This potential function is isotopically independent as are the two bond length functions. Thus in the DCN/CND fitting these three functions were held fixed at the HCN/CNH values and only the stretching vibration parameters were adjusted.

(a) The HCN/CNH Fit

The semirigid bender was first fitted to the HCN/CNH vibrational data given in Tables I, II, and IV. The calculated vibrational energies are rather insensitive to the

TABLE VI

The Experimental CND Vibrational Energies (in cm^{-1})

Stretching State (ν_1, ν_2)	Bending State ν_3	obs	obs-calc ^a	Ref.
(0,0)	0*	0	-	
	2*	733 ^b	0	
(0,1)	0*	1940	0	(29)
(1,0)	0*	2787	0	(2)

^aThe calculated values use the DCN/CND parameters of Tables VII, VIII, and IX.

^bEnergy estimated as described in Sect. III (d) of the text.

TABLE 7

Table VI CND Vibrational Energies: Observed and Calculated.

TABLE 8

Table VII HCN/CNH Ground State Bond Length Parameters.

TABLE VII

Bond Length Parameters as Fixed for Use in the Least Squares Fittings
of Both HCN/CNH and DCN/CND

Parameter	HCN	CNH
$r_{\text{Ha}} / \text{\AA}$	1.685	1.536
$r_{\text{CN}} / \text{\AA}$	1.150	1.169
$r_{\text{Ha}} / \text{\AA rad}^{-2}$	-0.970	-0.891
$r_{\text{CN}} / \text{\AA rad}^{-2}$	0.050	0.079

bond length functions, and, therefore, we use parameters specifying these functions that were fixed so as to model the ab initio values of (5). This was done by setting both r_{CN} and r_{Ha} , at both $\tau = 0$ and $\tau = \pi$, to the ab initio values; the four remaining parameters, r'_{CN} and r'_{Ha} at $\tau = 0$ and $\tau = \pi$, were fixed at values determined by a least squares fitting of the bond length functions to the ab initio values for bent geometries. These parameters are given in Table VII.

In the fitting to the experimental data we determined all six parameters that define the harmonic stretching frequencies ω_1 and ω_3 as functions of the bending angle. These functions are shown in Fig. 2 where, for comparison, the ab initio values of Perić and Mladenović (6) are also indicated. Although the ab initio values for ω_3 are systematically high it can be seen that the general forms of both of the ab initio functions are in good agreement with the experimental results reported here.

FIG. 2. The fitted harmonic stretching frequencies of HCN/CNH as a function of the angle τ . The ab initio values (6) are indicated by the open circles and triangles for ω_1 and ω_3 , respectively.

Figure 7: Fig. 2 The Harmonic Stretching Frequencies.

Due to the limited data available for the stretching overtones of CNH it was not possible to determine the functional forms of the x_{rn} . We therefore adjusted the x_{rn} but without allowing them to vary with r . This means that due to the large amount of data for HCN the anharmonic constants of CNH were effectively held at the HCN values and thus contaminate to some degree the harmonic constants obtained for CNH. All of the stretching vibration constants obtained in the HCN/CNH fitting are presented in the first column of Table VIII. Harmonic and anharmonic constants of HCN obtained by Maki (quoted in Ref. (33)) are given in the second column of this table.

In the fitting the barrier to isomerization H and the CNH-HCN energy difference ΔE were held fixed at the ab initio values of Pearson *et al.* (5). We note that the ab initio value of ΔE is in agreement with the recent experimental determination by Pau and Hehre (34). The HCN and CNH bending force constants were determined in the fitting and are presented in Table IX together with values obtained by other workers. The parameter τ_0 which specifies the bending angle corresponding to the maximum in the barrier was also determined and is also shown in Table IX. We feel, however, that τ_0 is in part acting as a shape parameter for the potential barrier and is not directly comparable to the ab initio value.

The true bending potential function V_0 that we have obtained is shown as the

Table VIII HCN/CNH Stretching Vibration Constants.

TABLE 9

TABLE VIII

Stretching Vibration Constants (in cm^{-1} except where noted) Determined in the Least Squares Fittings of HCN/CNH and of DCN/CND

Parameter	HCN		DCN	
	present work	Ref. (33) ^a	present work	Ref. (33) ^a
ω_1	3432.5(19) ^b	3442.3	2698.7(53)	2702.9
ω_3	2130.1(27)	2129.1	1949.2(53)	1953.2
ω_1^c	-1459(62)		-1590(83)	
ω_3^c	-277(78)		461(84)	
x_{11}	-49.24(25)	-52.69	-19.4(15)	-20.2
x_{33}	-9.62(34)	-11.58	-6.5(15)	-7.1
x_{13}	-17.75(50)	-13.08	-31.3(22)	-32.9
	CNH ^d		CND ^d	
ω_1	3810.0(32)		2869.0(47)	
ω_3	2061.4(42)		1961.8(47)	

^aValues for HCN and DCN obtained by conventional analysis by Dr. Maki (quoted in Ref. (33)) are shown here for comparison.

^bThe number in parentheses is one standard error in units of the last digit quoted for the parameter.

^cIn $\text{cm}^{-1} \text{rad}^{-2}$.

^dThe x_{rn} were held equal for HCN and CNH and for DCN and CND.

TABLE 10

Table IX HCN/CNH Constants of the True Bending Potential Function V_0 .

TABLE IX

Parameters of the True Bending Potential Function V_0 , Obtained by the Least Squares Fitting of HCN/CNH

Parameter	present work	Ref. (22)	Ref. (23)	Ref. (24)
$f_{\infty}(\text{HCN})$ /aJ rad ⁻²	0.2563(24) ^a	0.2596		0.263
$f_{\infty}(\text{CNH})$ /aJ rad ⁻²	0.0953(29)		0.1076	0.109
		Ref. (5)	Ref. (34)	
$\bar{\nu}$ /cm ⁻¹	(17319) ^b	17319		
τ_0 /degree	87.13(87)	73.7		
ΔE /cm ⁻¹	(5103) ^b	5103	5200±700	

^aThe number in parentheses is one standard error in units of the last digit quoted for the parameter.

^bFixed at the ab initio value of Pearson *et al.* (5).

lower curve in Fig. 2. The ab initio points calculated by Pearson *et al.* (5) are shown by the open circles. The upper curve in Fig. 2 is the effective bending potential V_{eff} for the stretching state $(v_1, v_2) = (0, 0)$. We have drawn horizontal lines on the appropriate sides of the barrier to represent the calculated pure bending energy levels of HCN and CNH. Levels included in the fit are drawn as solid lines and levels that are only calculated are drawn as dashed lines.

FIG. 3. The true bending potential function V_0 , obtained from the fitting to the HCN/CNH data, and the effective curve V_{eff} for the $v_1 = v_2 = 0$ state; the ab initio points (5) for V_0 are indicated by the open circles. The bending energy levels that are dashed are calculated but not observed.

Figure 8: Fig. 3 The HCN/CNH $\tilde{X}^1A'$ State True Bending Potential Function V_0 .

The HCN/CNH vibrational frequencies calculated with the optimized parameters (given in Tables VII, VIII, and IX) give the obs-calc values shown in Tables I, II, and IV. Note that the obs-calc differences for the fluorescence data given in Table II are consistent with the approximately 100 cm^{-1} uncertainty in the data.

(b) *The DCN/CND Fit*

Before fitting the vibrational levels of DCN/CND we used the true bending potential function determined from the HCN/CNH fitting to do a straight-through calculation of the pure bending levels of DCN/CND, not allowing for any variation in the stretching frequencies with bending angle. In this calculation we obtained 1138 cm^{-1} for the $2\nu_2^0$ level of DCN compared to the observed value of 1130 cm^{-1} , and for $2\nu_2^0$ of CND we calculated 751 cm^{-1} compared to the estimated experimental value of 733 cm^{-1} . Having satisfied ourselves about this agreement we proceeded to fit the DCN/CND data by varying only the stretching constants; the bending potential and the bond length functions were kept fixed at the final values used for HCN/CNH.

In the DCN/CND fitting we were able to determine the same nine stretching vibration parameters as were determined in the HCN/CNH fitting. That is we determined the six parameters that define the harmonic stretching frequencies ω_1 and ω_3 , as functions of the bending angle, and the three anharmonic constants x_{11} , x_{33} , x_{13} which were adjusted in the least squares fitting but not allowed to vary with τ . The stretching vibration parameters obtained in the fitting of DCN/CND are presented in the third column of Table VIII, followed by the harmonic and anharmonic constants of DCN obtained by Maki (quoted in Ref. (33)). The vibrational energies calculated with these parameters lead to the "obs-calc" entries in Tables V and VI.

V. SUMMARY

In this work we have used the semirigid bender model to study the bending isomerization of HCN into CNH and of DCN into CND. We have fitted all extant vibrational data for these molecules using a bending potential function together with stretching frequencies and bond lengths that depend on the bending angle. We are able to fit the bending energy levels satisfactorily for all four isotope-isomers using a true bending potential function with only three adjustable parameters.

We are presently writing a version of this program to study the $\bar{A}$ excited electronic state of the HCN/CNH system which has bent equilibrium configurations (27, 37). With the wavefunctions obtained from this work we plan to simulate the fluorescence and electronic spectra of the $\bar{A}-\bar{X}$ system, HCN; it is hoped that we will then be able to predict the appearance of the $\bar{A}-\bar{X}$ band system of CNH which has yet to be observed. Work is also continuing to include rotation in the model which would then allow the experimental determination of the bond length functions.

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TABLE 11

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Calculated vibrational ground state energy levels for HCN and CNH are given in Table 12 and Table 13 respectively. The **bold face** entries correspond to levels that have been seen in work in the ground state (or, for the (0,2°,0) level of CNH, a level derivable from such work) while those in *italics* correspond to levels seen in the $\tilde{A} \text{ } ^1\text{A}'' - \tilde{X} \text{ } ^1\text{A}'$ HCN fluorescence work of Baronavski [1979] and are thus only imprecisely known. The remaining entries in this table correspond to levels that have not yet been observed and obviously the uncertainty in the calculated energies increases as one goes further away from known values.

TABLE 12

HCN Calculated Ground State Vibrational Energies
(cm^{-1}).

		v_2 :	0	1	2	3	4	5	6
v_1	v_2								
$v_1 = 0$	0°	0	2099	4179	6239	8280	10302	12305	
	2°	1409	3501	5575	7629	9664	11679	13676	
	4°	2799	4886	6953	9001	11029	13039	15029	
	6°	4169	6250	8311	10353	12375	14379	16363	
	8°	5518	7593	9648	11684	13700	15697	17675	
	10°	6844	8912	10961	12991	15004	16992	18964	
	12°	8143	10205	12248	14272	16276	18261	20226	
	14°	9413	11470	13506	15524	17522	19500	21459	
	16°	10651	12701	14731	16742	18734	20706	22658	
	18°	11850	13893	15917	17921	19906	21871	23817	
	20°	13004	15040	17056	19054	21031	22989	24927	
$v_1 = 1$	0°	3308	5390	7451	9494	11517	13521	15506	
	2°	4685	6759	8815	10851	12868	14865	16844	
	4°	6043	8111	10161	12190	14201	16192	18164	
	6°	7382	9444	11487	13511	15515	17500	19466	
	8°	8700	10757	12793	14811	16809	18787	20747	
	10°	9995	12045	14076	16087	18079	20052	22005	
$v_1 = 2$	0°	6518	8581	10625	12650	14655	16642	18609	
	2°	7861	9917	11955	13973	15972	17952	19912	
	4°	9187	11237	13268	15280	17272	19245	21199	
	6°	10494	12538	14563	16568	18554	20521	22468	
$v_1 = 3$	0°	9629	11674	13700	15707	17695	19663	21612	
	2°	10937	12976	14995	16996	18977	20938	22880	
	4°	12230	14262	16275	18269	20243	22198	24133	
$v_1 = 4$	0°	12641	14668	16676	18665	20635	22586	24517	
	2°	13914	15935	17936	19918	21881	23825	25749	
	4°	15173	17187	19181	21157	23113	25049	26967	
$v_1 = 5$	0°	15553	17563	19553	21525	23477	25409	27323	
	2°	16791	18794	20777	22741	24686	26611	28518	
	4°	18015	20010	21987	23944	25882	27800	29700	
$v_1 = 6$	0°	18367	20358	22331	24285	26219	28134	30029	
	2°	19568	21552	23518	25464	27390	29298	31186	
	4°	20756	22733	24691	26630	28550			

TABLE 13

CNH Calculated Ground State Vibrational
Energies (cm^{-1}).

		v_2 :	0	1	2	3
		v_1				
$v_1 = 0$	0°	0	2029	4039	6030	
	2°	932	2954	4957	6940	
	4°	1904	3919	5916	7893	
	6°	2903	4913	6904	8875	
$v_1 = 1$	0°	3665	5676	7668	9640	
	2°	4530	6534	8518	10483	
	4°	5443	7440	9418	11376	
	6°	6389	8381	10352	12305	
$v_1 = 2$	0°	6706				

Chapter III

THE $\tilde{A}^1A''$ EXCITED ELECTRONIC STATE OF HCN/CNH

The $\tilde{A}^1A''$ first excited electronic state of HCN has been studied in detail by Herzberg and Innes [1957] who investigated the high resolution $\tilde{A}-\tilde{X}$ absorption spectrum of this molecule. Further work on this system was later done by Bunker and Stone [1972]. From these studies it is clear that in the $\tilde{A}^1A''$ state the equilibrium structure of HCN is bent, with a bond angle of 120.9° (BS).

The $\tilde{A}^1A''$ first excited state of CNH has not yet been observed experimentally although it has been looked for at NRC. By *ab initio* calculations Laidig and Schaefer have determined that in the $\tilde{A}^1A''$ state CNH is also bent at equilibrium, with a bond angle of 109.3° . More interesting, they have determined that in the $\tilde{A}^1A''$ excited state the CNH potential energy minimum lies about 5000 cm^{-1} below that of HCN, as opposed to the $\tilde{X}^1A'$ ground state where the CNH potential minimum lies about 5000 cm^{-1} above that of HCN.

The experimentally determined bending levels of the $\tilde{A}^1A''$ excited state of HCN were used to do a least squares fitting of the semirigid bender model. In this fitting all of the CNH, and some of the HCN, parameters had to be held fixed at *ab initio* values.

In this work the vibrational levels of the $\tilde{A}$ 'A' excited state of HCN/CNH are labelled according to the modern convention (Herzberg [1966]), $(v_1, v_2, v_3)^K$, where v_1 is the quantum number for the "H" stretching vibration (C-H stretch for HCN and N-H stretch for CNH), v_2 is the *bent convention* bending quantum number, and v_3 is the quantum number for the C-N stretching vibration. K is the unsigned quantum number for rotation about the molecule fixed z-axis (the axis of linearity).

3.1 PARAMETERIZATION

Due to the bent geometries of the $\tilde{A}$ 'A' excited state equilibrium configurations of HCN and of CNH, the parameterization used in studying this state had to be modified from that used in the ground state. The natural parameters to use are the equilibrium values of the relevant quantities. These, however, proved insufficient for the bond length parameterization as is discussed below. The description of the double minimum potential function with bent equilibria requires more parameters than that with linear equilibria and thus the parameters of the potential function also had to be modified. Stretching vibrations were not included in this study as there is not enough experimental data to allow their effects to be determined.

3.1.1 Bond Lengths

As was the case for the ground state it is not reasonable to attempt to determine the bond length functions in a least squares fitting involving only vibrational data. For the excited state of HCN/CNH, however, an *ab initio* calculation of the complete bending isomerization has not yet been done. What are available are the HCN $\tilde{A}^1A'$ experimental geometries of Herzberg and Innes [1957] and of Bunker and Stone [1972] (whose values are used here), and the CNH $\tilde{A}^1A'$ *ab initio* geometries of Laidig and Schaefer [1983].

The parameters chosen to represent the molecular geometry were the bond lengths at the HCN and CNH equilibria and the bond angles of these equilibria. These six parameters are illustrated in Fig. 9.

Initial attempts to use these parameters with linear series ($n_{\text{max}} = 1$ in the series expansion Eq. 14) for the bond length functions resulted in unreasonable values for these functions at the linear limits $\tau = 0$ and $\tau = \pi$. Instead a cubic series ($n_{\text{max}} = 3$) had to be used with the bond lengths at the linear configurations being the additional parameters. For this work the bond lengths at the linear configurations were fixed to the values at the equilibrium configurations. These values are given in Table 14.

TABLE 14
HCN/CNH $\tilde{A}$ "A" State Bond Length
Parameters.

as Fixed for Use in the Least
Squares Fitting of HCN/CNH.

Parameter	HCN	CNH
$r_{\text{CN}}^e / \text{\AA}$	1.297	1.433
$r_{\text{CH}}^e / \text{\AA}$	1.140	
$r_{\text{NH}}^e / \text{\AA}$		1.036
α_e / deg	120.9	109.3

One consequence of this choice of parameters is that the relationship between them and the expansion coefficients for $r_{\text{Ha}}(\tau)$ and $r_{\text{CN}}(\tau)$ is not linear. This is due to the non-linear relationship between ρ and τ and hence the bond angle (which, for HCN, is the complement of ρ). Given the input bond length parameters the computer program had, therefore, to use an iterative multidimensional Newton-Raphson technique to solve for the coefficients actually used in the power series expansions for r_{Ha} and r_{CN} .

3.1.2 Potential Function

As seen in Fig. 10, ten parameters were used to represent the bending potential function of the excited state. These consist of three barrier energies,

1. $H(\text{HCN})$ the barrier to linearity of HCN,
2. $H(\text{CNH})$ the barrier to linearity of CNH, and
3. H_0 the barrier to internal rotation, measured from the HCN minimum;

two energy differences,

4. E_0 the energy difference between the potential energy minima of the $\tilde{X}^1A'$ ground state and the $\tilde{A}^1A''$ excited state of HCN, and
5. ΔE The difference, in the $\tilde{A}^1A''$ excited state, between the HCN and the CNH minima (CNH - HCN energy);

two force constants,

6. $f_{\alpha\alpha}$ (HCN) the HCN bending force constant, and
 7. $f_{\alpha\alpha}$ (CNH) the CNH bending force constant;
- and three angles,
8. τ (HCN) the value of τ corresponding to the HCN minimum,
 9. τ (CNH) the value of τ corresponding to the CNH minimum, and
 10. τ_0 the value of τ corresponding to the barrier to internal rotation.

The expressions for the bending force constants in terms of the power series coefficients of Eq. 14 are rather more complicated than they were in the ground state but again,

$$f_{\alpha\alpha} = \left(\partial^2 / \partial \tau^2 V(\tau) \right) \left(\partial \tau / \partial \alpha_x \right)^2 \Big|_{\tau_x}, \quad (22)$$

where $x = \text{HCN or CNH}$, and α_x is the true bond angle for the x configuration, as was shown in Fig. 9. These two expressions are treated in the same way as was done for the ground state.

The τ values corresponding to the HCN and CNH minima are determined from the input bond length parameters shown in Fig. 9 and are therefore not treated as parameters in the least squares adjustment of the potential function to the experimental data.

3.1.3 Stretching Frequencies

The only experimentally observed non-rotational ($K=0$) stretching level seen in the $\tilde{A}$ 'A' excited state is the $(v_1, v_2) \equiv (0, 1)$ stretching state of HCN. Due to this lack of data on stretching levels only bending levels were fitted

in the study of the excited state and thus the stretching vibration contribution to the effective potential had to be ignored. The bending potential function obtained from the least squares fitting is therefore the effective bending potential function V_{eff} of the $(v_1, v_2) = (0, 0)$ stretching state.

3.2 DATA AND RESULTS

The bending energies of the $\tilde{A}^1A'$ excited state of HCN are taken from the ultraviolet absorption work of Herzberg and Innes [1957] and are reported in the "obs" column of Table 15. The first entry in this table is the energy of the HCN $\tilde{A}^1A'$ $(0, 0, 0)^0$ level, referred to the HCN minimum of the ground state bending potential function; this is the sum of the zero-point energy of the bending vibration in the ground state 702.2 cm^{-1} (determined in the study of the ground state), the energy $v_2[\tilde{X}^1A'(0, 1^1, 0) \text{ HCN}] - B = 712.0 \text{ cm}^{-1}$ from Wang and Overend [1973], and the energy difference $v_2[\tilde{A}^1A'(0, 0, 0)^0 - \tilde{X}^1A'(0, 1^1, 0)] = 51544.9 \text{ cm}^{-1}$ of Herzberg and Innes [1957].

No experimental data are available for the $\tilde{A}^1A'$ state of CNH.

The semirigid bender model was fitted, by least squares adjustment of four of the bending potential function parameters, to the observed pure bending energies presented in Table 15. In this fitting the barrier to linearity and the

TABLE 15

HCN $\tilde{A}$ 'A' State Vibrational Energies:
Observed and Calculated (cm^{-1}).

Level	obs	calc	obs-calc
$(0,0,0)^0$	52959.1	52959.1 ^a	0.0
$(0,1,0)^0$	938.3	937.6	0.7
$(0,2,0)^0$	1857.5	1857.6	-0.1
$(0,3,0)^0$	2755.5	2755.8	-0.3
$(0,4,0)^0$	3626.2	3626.4	-0.2
$(0,5,0)^0$	4460.8	4460.2	0.6
$(0,6,0)^0$	5240.7	5240.9	-0.2

^aThe $(0,0,0)^0$ energy level is referred to the HCN $\tilde{A}$ ' ground state potential minimum. All other levels are referred to the $(0,0,0)^0$ level of the HCN $\tilde{A}$ " state.

bending force constant for HCN were determined. These quantities have previously been roughly determined by Bunker and Stone [1972] whose values are included in Table 16, with the present values, for comparison. The excited-ground state energy difference E_0 and the angular position of the barrier to internal rotation τ_0 were also determined. As was the case in the ground state fitting, it is felt that this latter parameter is in some sense acting as a shape parameter for the potential barrier.

TABLE 16

HCN/CNH $\tilde{A}^{+1}A''$ State: Constants of the Effective
Bending Potential Function V_{eff} .

Parameter	Present Work	Bunker and Stone (1972)
$H_{\text{HCN}}/\text{cm}^{-1}$	6602(19) ^a	6533
$H_{\text{CNH}}/\text{cm}^{-1}$	5000 ^b	
H_0/cm^{-1}	12500	
E_0/cm^{-1}	52496.0(6)	
$\Delta E/\text{cm}^{-1}$	-5000	
$f_{\alpha\alpha}(\text{HCN})$ /aJ rad ⁻²	.5682(9)	.5677
$f_{\alpha\alpha}(\text{CNH})$ /aJ rad ⁻²	.65	
τ_0/deg	88.4(2)	

^aThe number in parenthesis is one standard error
in units of the last digit quoted for the parameter.

^bParameters quoted without errors were held fixed
in the least squares fitting.

The four remaining parameters were held fixed at either *ab initio* or chosen values. In particular, the CNH-HCN energy separation was fixed at -5000 cm^{-1} to correspond with the *ab initio* value of Laidig and Schaefer [1983] of $-4870 \pm 2000 \text{ cm}^{-1}$. The $\tilde{A} \text{ } ^1A''$ state bending force constant of CNH (0.65 aJ rad^{-2}), was obtained by scaling the *ab initio* value (0.80 aJ rad^{-2}) of Laidig and Schaefer [1983] by a factor determined from a comparison of their calculated bending frequencies with the experimentally determined frequencies for the $\tilde{A} \text{ } ^1A''$ and $\tilde{X} \text{ } ^1A'$ states of HCN and the $\tilde{X} \text{ } ^1A'$ state of CNH.

The CNH barrier to linearity was chosen as 5000 cm^{-1} and the HCN/CNH barrier to internal rotation was fixed by setting the maximum barrier approximately equal to the barrier in the ground state: $12500 + 5000 = 17500 \text{ cm}^{-1}$ compared with the *ab initio* barrier in the ground state of 17319 cm^{-1} (Pearson, Schaefer, and Wahlgren [1975]).

The final parameters of the bending potential function are presented in Table 16. The excited state bending potential function derived from these constants is shown in Fig. 11, along with the calculated HCN and CNH energy levels. The energies calculated from this potential function are shown in the "calc" columns of Table 15 and Table 17 and can be seen to be in excellent agreement with the observed energies (Table 15).

TABLE 17

CNH $\tilde{A}^1A''$ State Vibrational
Energies: Calculated (cm^{-1}).

Level	calc
$(0,0,0)^0$	48042 ^a
$(0,1,0)^0$	1074
$(0,2,0)^0$	2078
$(0,3,0)^0$	2996
$(0,4,0)^0$	3794
$(0,5,0)^0$	4429
$(0,6,0)^0$	5038

^aThe $(0,0,0)^0$ energy is referred to the HCN $\tilde{X}A'$ ground state potential minimum. All other levels are referred to the $(0,0,0)^0$ level of the CNH $\tilde{A}A''$ state.

Chapter IV

TRANSITION INTENSITIES

The $\tilde{A}$ - $\tilde{X}$ electronic transition of HCN is known to give rise to a long progression in the bending vibration, both in absorption (Herzberg and Innes [1957]) and emission (Baronavski [1979]). This is due to the difference in geometry of the two states as is illustrated in Fig. 12 which shows the complete bending potential function for both the $\tilde{X}$ 'A' ground and the $\tilde{A}$ 'A' excited states of HCN/CNH. From this figure it is clear that the HCN and CNH potential minima change significantly on electronic excitation. Thus, when an electronic transition occurs (which happens on a time scale which is much shorter than that of the vibrational motion), the molecule "finds itself" in a geometry which, in the new electronic state, is far removed from equilibrium and is thus vibrationally excited. This effect is qualitatively described by the "Franck-Condon Principle" and is quantified by the calculation of quantum mechanical transition probabilities as is discussed below.

The goal of the work reported in this chapter was to use the semirigid bender wavefunctions obtained from the study of the $\tilde{X}$ 'A' ground and the $\tilde{A}$ 'A' excited states of HCN/CNH to calculate relative intensities for various vibrational

bands appearing in the electronic spectrum of HCN/CNH. The purpose of this was twofold: first to determine if such a calculation generated reasonable results (which would imply that the transition intensities were well explained by the current model), and second, if the calculated intensities for HCN did appear to be in reasonable agreement with the observed intensities, to *predict* the relative intensities for CNH. It is important to emphasize that the intensities which are reported here were calculated entirely on the basis of the wavefunctions obtained from the least squares fittings of the transition frequencies - *no fitting to observed intensities was done.*

The $\tilde{A}-\tilde{X}$ electronic transition is an electric dipole moment transition and as such the intensity of an individual vibrational band in this transition is proportional to the product of the following four factors (see, for example, pp. 18-21 of Herzberg [1950]):

1. The population of the initial state.
2. The modulus squared of the transition moment matrix element.
3. A frequency factor, ν' for spontaneous emission, and ν for absorption (these factors are ν' and 1 when the intensity is measured in photon number rather than in energy).
4. A proportionality constant which, as only relative intensities are being calculated, is of no importance here.

The first two of these factors require a more detailed discussion.

1) *Population*. For the emission spectra which will be considered here, only a single excited state is involved for each spectrum. The population factor is therefore constant and may be included in the proportionality constant (4).

In the electronic absorption spectrum of HCN several hot bands are seen and the *relative* populations are important. The relative populations of the various ground state levels are given by the well known Boltzmann factor $e^{-E/kT}$ where E is the energy of the state and T is the temperature of the gas. As only the *relative* population factor is important, the energy of the vibrational ground state was chosen as the zero of the energy scale.

2) *Matrix Element*. The quantum mechanical amplitude for an electric dipole moment transition (ignoring the other factors listed above) between a state Ψ' and a state Ψ'' is

$$A = \langle \Psi' | \mathbf{E} \cdot \mathbf{M} | \Psi'' \rangle$$

(23)

where $\mathbf{E}$ is the electric field vector of the incident or emitted radiation and $\mathbf{M}$ is the molecular dipole moment. For visible and ultraviolet radiation the wavelength of the light involved is many hundreds of times larger than the

size of the molecule and we may remove the electric field from the matrix element. As the electronic spectra of HCN/CNH that are considered in the present work were obtained in the gas phase, the relative orientation of the electric field and the molecules is random. The average of the square modulus of the electric field may therefore be absorbed into the constant factor (4) when the transition probability is calculated, as this is done by taking the square of A and then averaging over all molecules. The square modulus of the transition amplitude may therefore be written as

$$|A|^2 = |\langle \Psi' | M | \Psi'' \rangle|^2 \quad (24)$$

The work involved in calculating intensities therefore consists of evaluating the matrix elements of the dipole moment operator, and it is this that is discussed for the remainder of this section.

Recalling, from Chapter I, that the vibration-rotation wavefunctions in the semirigid bender approximation are written as a product of stretching, bending, and z-rotation wavefunctions (as the rotation about the z- or a-axis is enough to characterize the vibrational levels of interest the end-over-end rotation will not be considered here) a

"complete" molecular wavefunction can be obtained by adding an electronic part to the product,

$$\begin{aligned}\Psi &= \psi_e \psi_b^K(\rho) \psi_s^\tau(Q_1, Q_2) \psi_{\text{rot}}, \\ &= \psi_e \psi_v^K \psi_{\text{rot}}.\end{aligned}\quad (25)$$

The space fixed components of M , which are labelled M_ζ , $\zeta = X, Y, Z$ (the space fixed axes), can be written in terms of the molecule fixed components M_α , $\alpha = x, y, z$ (the molecule fixed axes) by the use of the direction cosine elements, as is described, for example, in Bunker [1979],

$$\begin{aligned}M_\zeta &= \lambda_{x\zeta} M_x + \lambda_{y\zeta} M_y + \lambda_{z\zeta} M_z \\ &= \sum_\alpha \lambda_{\alpha\zeta} M_\alpha, \quad \alpha = x, y, z,\end{aligned}\quad (26)$$

where the direction cosine elements are dependant only on rotational coordinates. Substitution of this expression, along with the product basis set, into the transition amplitude matrix element gives three vector component amplitudes,

$$A_\zeta = \sum_\alpha \langle \psi'_{\text{rot}} | \lambda_{\alpha\zeta} | \psi''_{\text{rot}} \rangle \langle \psi'_v \psi'_e | M_\alpha | \psi''_e \psi''_v \rangle, \quad (27)$$

(see Eq. 11-156 of Bunker [1979]).

Remembering that from the Born-Oppenheimer separation the electronic wavefunctions are parametrically dependant on the nuclear coordinates (ρ, Q_1, Q_2) , an integration over the electronic coordinates, at a given nuclear configuration, gives,

$$M_{\alpha}^{e'e''}(\rho, Q_1, Q_2) = \langle \psi_e' | M_{\alpha} | \psi_e'' \rangle, \quad (28)$$

As the symmetries of the $\tilde{X}$ and $\tilde{A}$ states of HCN/CNH are A' and A'' , respectively, the vanishing integral rule thus requires that for $M_{\alpha}^{e'e''}$ to be non-zero, the symmetry of M_{α} must be A'' . However (Eq. 11-161 of Bunker [1979]) $\Gamma(M_{\alpha}) = \Gamma(T_{\alpha})$ and from Table A-1 (*ibid.*) only T_C has symmetry A'' . The non-zero electric dipole transition moment thus lies along the c -axis - which is perpendicular to the axis of linearity (the a -axis). This transition is thus an example of what is known as a "perpendicular" transition and has "c-type" selection rules. C-type bands have the selection rule on K : $\Delta K = \text{odd}$, with the predominant transitions governed by $\Delta K = \pm 1$. As the K rotational quantum number is sufficient to characterize the vibrational levels of HCN/CNH we can replace the rotational matrix element with a Kronecker delta function, $\delta_{K', K'' \pm 1}$.

The transition moment $M_C^{e'e''}(\rho, Q_1, Q_2)$ may be expanded in terms of the normal coordinates Q_1 and Q_2 (chosen from one of the two electronic states, e' or e''). The dependence of the electronic dipole transition moment on Q_1 and Q_2 , i.e. the electrical anharmonicity involving Q_1 and Q_2 , is neglected. As only one pair of electronic states is being considered the notation may now be simplified by writing this term as $M_C(\rho)$.

For the $\tilde{A}-\tilde{X}$ transition of HCN/CNH the transition moment function $M_C(\rho)$ is not known, although some *ab initio* work is aimed in this direction (Schaefer [1983]). Some deduction, however, can be made on the general form of this function. As the $\tilde{X}$ 'A' ground state correlates at linearity to a Σ^+ state (Herzberg and Innes [1957]), while the $\tilde{A}$ 'A' state correlates to a linear Δ state (*ibid.*) the electronic dipole transition is forbidden at the linear configurations (for both HCN and CNH). To model this behaviour the transition moment was written

$$M_C = \sin \tau,$$

(29)

Test calculations were done with $M_C = \tau$, and $\sin \tau$, and it was found that the calculated relative intensities for HCN emission and absorption were almost unchanged. It was therefore felt that a calculation of absorption and emission intensities for HCN and CNH done using $M_C = \sin \tau$ would be satisfactory. In any case, the lack of any other information on the form of M_C does not allow much choice in the matter.

The transition amplitude A_C has thus been reduced to the form,

$$A_C = \delta_{K', K'' \pm 1} \langle \psi_V'(\rho, Q_1, Q_2) | M_C(\rho) | \psi_V''(\rho, Q_1, Q_2) \rangle.$$

(30)

In the calculation of this transition amplitude the factors appearing in the integrand should, in principle, each be evaluated at the same nuclear configuration at each point in the integration. This would require the knowledge of the complete vibrational wavefunction as a function of the three vibrational degrees of freedom, or, equivalently, the evaluation of the complete stretching vibration part of the wavefunction at each value of the bending angle. This is not currently feasible and instead some approximation must be made. As the "H" stretching vibration ν_1 is not active in the electronic transition - only one band involving this vibration has been observed (Bunker and Stone [1972]) - this vibration can be neglected in the calculation of transition amplitudes. The C-N stretching vibration, however, is very apparent and long progressions in this vibration are seen in both emission and absorption. Fortunately the C-N bond stretching vibration is *not* strongly dependant on the bending angle in the $\tilde{X}^1A'$ state (see the lower curve in Fig. 7) and it was therefore reasonable to further approximate the complete vibrational wavefunction in the $\tilde{X}^1A'$ state by evaluating the C-N stretching vibration part of the wavefunction at the equilibrium bending angle τ_e , i.e. at the nuclear configurations shown, to scale, in Fig. 13. The complete vibrational wavefunctions used in the calculation of the transition moment are thus approximated by,

$$\begin{aligned}\psi_v(\rho, Q_1, Q_2) &= \psi_b(\rho) \psi_s^T(Q_1, Q_2) \\ &= \psi_b(\rho) \psi_s^{Te}(Q_1=0, Q_2),\end{aligned}\quad (31)$$

where the "H" stretching vibration is neglected and the C-N stretching wavefunctions are evaluated at the equilibrium bending angle. In the $\tilde{A}$ 'A' state the C-N stretching vibration is strongly dependant on the bending angle and therefore only $(v_1, v_2) = (0, 0)$ levels of this state are included in the intensity calculations. This is discussed in more detail in Section 4.1.1.

The transition amplitude now has the form,

$$\begin{aligned}A_C &= \delta_{K', K'' \pm 1} \langle \psi_b'(\rho) | M_C(\rho) | \psi_b''(\rho) \rangle \\ &\times \langle \psi_s'(Q_2) | \psi_s''(Q_2) \rangle,\end{aligned}\quad (32)$$

where the last factor is the Franck-Condon factor for the C-N stretching vibration. Due to the small dependance of the C-N stretching vibration on the bending motion the neglect of the dependance of this factor on the bending angle is not felt to be a significant source of error. It should be noted that the stretching wavefunctions that now appear in this factor are evaluated at *different* geometries of the molecule, corresponding to the different equilibrium values of the bending angle in the two electronic states involved in the transition. The calculation of the stretching wave-

functions and of their Franck-Condon factors is described in the next section.

The evaluation of the bending-wavefunction matrix elements requires a brief discussion. As the semirigid bender wavefunctions are obtained from a Hamiltonian derived with a volume element $d\rho\,dQ_1\,dQ_2$, the integration of the bending matrix element had to be done in terms of ρ . This was done by integrating in terms of the ρ of one state. For each

value of ρ in the integration the angle τ in this state was then calculated and the wavefunction of the other state was evaluated, by numerical interpolation, at the point corresponding to the same value of τ . Those absorption (up) and emission (down) transitions, for the lowest lying bending levels, which had the largest calculated bending overlaps, are indicated in Fig. 12 by the vertical arrows and can be seen to obey the qualitative Franck-Condon principle very well.

From the calculated bending-vibration transition-moment matrix elements and the stretching vibration Franck-Condon factors it was then possible to calculate A_C and thus the relative intensities. The next section describes the calculation of the stretching wavefunctions and their Franck-Condon overlaps.

4.1 STRETCHING WAVEFUNCTIONS

The Schrödinger Equation for the C-N stretching vibration, for example, is,

$$-\frac{\partial^2}{\partial r^2} \psi(r) = \frac{2}{\hbar^2 \mu} [E - V(r)] \psi(r), \quad (33)$$

where,

$$1/\mu = 1/m_C + 1/m_N,$$

and where r is the C-N bond length and m_C and m_N are the atomic masses of the Carbon and Nitrogen atoms. A power se-

ries in $(r - r_e)$ is used to represent the potential function,

$$V(r) = \frac{1}{2} f_{11}(r-r_e)^2 + \frac{1}{6} f_{111}(r-r_e)^3 + \frac{1}{24} f_{1111}(r-r_e)^4. \quad (34)$$

The first coefficient f_{11} in this series is related to the harmonic stretching frequency ω_1 by,

$$f_{11} = 4 \pi^2 c^2 \omega_1^2 / \mu. \quad (35)$$

The higher order force constants were estimated from the harmonic constant f_{11} by using the factors of Kuchitsu and Morino [1965] as is described below.

The stretching vibration Schrödinger equation was solved using the technique of Numerov-Cooley numerical integration (Appendix B) to obtain both its eigenvalues and eigenfunctions. The wavefunctions that were obtained were used to calculate Franck-Condon factors for both the v_1 and v_2 stretching vibrations, in absorption and emission, for both HCN and CNH. Each of these vibrations is now discussed in turn.

4.1.1 C-N Stretching Vibration.

To calculate the harmonic force constant f_{11} for the C-N stretching vibration of the $\tilde{X}^1A'$ states of HCN and CNH the harmonic C-N stretching frequencies of Ross and Bunker [1983] (see also Chapter II) were used. The experimental C-N stretching frequency of 1506 cm^{-1} of Herzberg and Innes [1957] was used for the $\tilde{A}^1A''$ state of HCN while the *ab initio* frequency of Laidig and Schaefer [1983], after being decreased by the factor 1.1 (estimated from a comparison of experimental frequencies with other of their calculated frequencies), was used for the $\tilde{A}^1A''$ state of CNH.

The f_{11} and f_{111} potential constants were obtained by using the a_1 and a_2 factors for CN given by Kuchitsu and Morino [1965]. For the C-N stretching vibration $a_1 = 2.268\text{ \AA}^{-1}$ and $a_2 = 2.294\text{ \AA}^{-1}$. Jensen, Bunker, and Hoy [1982] give the following relationships that allow the determination of f_{11} and f_{111} ,

$$\begin{aligned} f_{11} &= -3 a_1 f_{111} \\ f_{111} &= 7 a_2^2 f_{11} \end{aligned}$$

(36)

The complete set of constants used for the C-N stretching vibrations is presented in Table 18.

The C-N equilibrium bond lengths used in the potential function expansions are presented in Table 19. The $\tilde{X}^1A'$ state bond lengths of HCN and of CNH are from the *ab initio*

TABLE 18

HCN/CNH C-N Stretching Vibration: Potential
Function Constants.

Constant	Molecule	State	
		$\tilde{A}'$	$\tilde{A}''$
ω_3^f /cm ⁻¹	HCN	2130	1506
	CNH	2061	1086
f_{33}^a /aJ Å ⁻²	HCN	17.274	8.636
	CNH	16.173	4.491
f_{333} /aJ Å ⁻³	HCN	-117.533	-58.756
	CNH	-110.042	-30.554
f_{3333} /aJ Å ⁻⁴	HCN	636.328	318.106
	CNH	595.769	165.418

^aThe f_{33} values are calculated directly
from the ω_3 values.

work of Pearson, Schaefer, and Wahlgren [1975]. The $\tilde{A}'$ $\tilde{A}''$ C-N bond length of HCN is from the empirical work of Bunker and Stone [1972] while that for CNH is from the *ab initio* work of Laidig and Schaefer [1983].

TABLE 19
HCN/CNH C-N Equilibrium Bond
Lengths.

Molecule		State	
		$\bar{r}_{A'}$	$\bar{r}_{A''}$
$r_{CN} / \text{\AA}$	HCN	1.150	1.297
	CNH	1.169	1.433

With the potential functions thus specified the Schrödinger equation was solved by Numerov-Cooley numerical integration between the bond limits of 0.7 Å and 2.1 Å for HCN and between the bond limits of 0.7 Å and 2.3 Å for CNH. These ranges were subdivided into a grid of 500 points in the numerical integration and were chosen to ensure that the height of the potential function at the limits of integration was at least ten times higher than the highest eigenvalue of interest. (This condition is given in Jensen [1983a]). Some of the C-N stretching frequencies calculated in this manner are given in Table 20. For comparison observed values, where available, are also given, along with energies taken from Table 12 and Table 13 which were calculated using the semirigid bender model as described in Chap-

ter II. For the $\tilde{X}$ 'A' ground state of HCN and CNH the observed values are from infrared work and are taken from Table I and Table IV respectively. The observed values for the $\tilde{A}$ 'A' excited state of HCN were obtained using the empirical formula of Herzberg and Innes [1957], $\nu_1(0,0,v_1)^1 = 1505.9 \nu_1 - 10.0 \nu_1^2 \text{ cm}^{-1}$ and by using their value $(A-B) = 21.6 \text{ cm}^{-1}$ to calculate the values $\nu_1(0,0,v_1)^0$.

The general agreement of the C-N stretching energies calculated here, with both the observed and semirigid bender energies, can be seen to be quite good. It is therefore expected that the stretching wavefunctions, and the Franck-Condon factors calculated from them, are reasonably reliable for low lying stretching states.

The C-N stretching potential functions along with some of their calculated energy levels are shown in Fig. 14 and Fig. 15 for HCN and CNH respectively. It is clear in the second of these figures that the change in C-N bond length between the $\tilde{X}$ 'A' ground and the $\tilde{A}$ 'A' excited states is considerable for the CNH configuration. Because of this, the calculated Franck-Condon factors for absorption from the ground state of CNH do not reach a maximum until $v_1 \geq 9$. At this highly excited stretching level the calculations involve an unreasonably long extrapolation beyond known or *ab initio* levels. The calculated Franck-Condon factors for absorption from the $\tilde{X}$ 'A' ground state are given in Table 21 while those for emission from the $\tilde{A}$ 'A' excited state are given in

TABLE 20

HCN/CNH C-N Stretching Frequencies: Observed and
Calculated (cm^{-1}).

State	Molecule	v_3	obs ^a	SRB ^b	Anh ^c
$\bar{X}A'$	HCN	0	0	0	0
		1	2097	2099	2105
		2	4173	4179	4188
		3		6239	6250
		4		8280	8296
		5		10302	10327
		6		12305	12347
	CNH	0	0	0	0
		1	2029	2029	2036
		2		4039	4050
		3		6030	6044
		4		8001	8021
$\bar{A}A''$	HCN	0	0		0
		1	1474		1482
		2	2950		2943
		3	4406		4386
		4	5842		5818
	CNH	0			0
		1			1063
		2			2107
		3			3138
		4			4162

^aSee text for the sources of these values.

^bCalculated using the SemiRigid Bender model as described in Chapter II.

^cCalculated using the Numerov-Cooley technique and the anharmonic potential functions as described in the text.

Table 22. The absorption (up) and emission (down) transitions which had the strongest calculated C-N stretching vibration Franck-Condon factors are indicated in Figs. 14 and 15 by the vertical arrows.

The use of these Franck-Condon factors in the calculation of absorption and emission intensities requires some discussion.

The excited stretching vibration levels involved in the absorption transitions are those in the $\tilde{A}$ $^1A''$ state. In this state, however, it was only possible to determine the effective potential function for the $(v_1, v_2) = (0, 0)$ stretching state (Chapter III). For the $\tilde{A}$ $^1A''$ state bending wavefunctions are therefore only available for this ground stretching vibration state. Also, the variation with bending angle of the harmonic stretching frequency ω_1 is quite significant in the $\tilde{A}$ $^1A''$ excited state (see Table 18), whereas this variation is neglected in the calculation of the transition moments (see Eqs. 31 and 32). Finally, the $\tilde{A}$ $^1A''$ state of HCN is predissociated, with the excitation of v_1 greatly accelerating the predissociation (Herzberg and Innes [1957]). Due to this dissociation, transitions to $\tilde{A}$ $^1A''$ state levels involving the v_1 vibration become progressively more diffuse with increasing v_1 and as a result the estimation of the experimental intensities from the plate darkening becomes even more approximate. For these three reasons absorption intensities were only calculated

Figure 14: The C-N Stretching Potential Function for HCN.

TABLE 21

HCN/CNH C-N Stretching Vibration:
Franck-Condon Absorption Factors.

Transition $v_3'' = 0, v_3'$	$ \langle v_3'' v_3' \rangle ^2$	
	HCN	CNH
0	.0234	.0000401
1	.0735	.000289
2	.126	.00112
3	.158	.00312
4	.161	.00696
5	.142	.0132
6	.111	.0233
7	.0794	.0339
8	.0526	.0473
9	.0326	.0612
Total ^a	.960	.190

^aThis total represents the fraction of the total intensity accounted for by the transitions included in the sum.

for bending transitions. The results of these calculations are presented in Section 4.2.

In the emission spectra that are considered below, the only excited v , levels that are involved are in the $\tilde{X}^1A'$

TABLE 22

HCN/CNH C-N Stretching Vibration:
Franck-Condon Emission Factors.

Transition $v_3' = 0, v_3''$	$ \langle v_3' v_3'' \rangle ^2$	
	HCN	CNH
0	.0234	.0000401
1	.100	.000488
2	.199	.00283
3✓	.241	.0104
4	.204	.0275
5	.122	.0554
6	.0646	.0894
7	.0266	.119
8	.00944	.136
9	.00299	.135
Total ^a	.993	.576

^aThis total represents the fraction of the total intensity accounted for by the transitions included in the sum.

ground state for which the effective potential function, and therefore the bending wavefunctions, are known for arbitrary stretching states (v_1, v_2) (Chapter II). Also, the variation with bending angle of ω , in the $\tilde{X}$ 'A' state is rather small

(Fig. 7 and Table 18) and the neglect of this variation in Eqs. 31 and 32 should be of minor importance. * the emission, the effects of the predissociation will be the same for all transitions and can therefore be neglected in the calculation of relative intensities. For these three reasons the emission intensities of transitions involving stretching, as well as bending, vibrational excitation, were calculated and are presented in Section 4.3.

4.1.2 "H" Stretching Vibration.

The "H" stretching vibration Franck-Condon factors were calculated, using the same technique as was used for the C-N stretching vibration, to understand the lack of bands involving ν_1 in the observed electronic spectra. For this the harmonic C-H stretching frequency of HCN and the harmonic N-H stretching frequency of CNH were taken from Ross and Bunker [1983] (see Table VIII), while for the $\tilde{A}^1A'$ excited state the empirical value of Bunker and Stone [1972] is used for HCN and the *ab initio* value of Laidig and Schaefer [1983] (reduced by the factor 1.1 as described in the section above) is used for CNH. The higher order force constants were calculated using the parameters of Kuchitsu and Morino [1965] as was described above (see Eq. 36). The set of potential function constants that were thus determined, and were then used in the calculations, are given in Table 23.

* As the upper state is common for all transitions in ...

22
OF / DE

TABLE 23

HCN/CNH "H" Stretching Vibration: Potential
Function Constants.

Constant	Molecule	State	
		$\bar{\nu}$ A ⁻¹	$\bar{\nu}$ A ⁻¹
ω_1 /cm ⁻¹	HCN	3432	3123
	CNH	3810	3283
f_{11}^a /aJ Å ⁻²	HCN	6.452	5.343
	CNH	8.041	5.970
f_{111}^b /aJ Å ⁻³	HCN	-38.346	-31.752
	CNH	-52.829	-39.225
f_{1111}^c /aJ Å ⁻⁴	HCN	196.724	162.894
	CNH	292.602	217.254

^aThe f_{11} values are calculated directly from the ω_1 values.

^bThe f_{111} values are calculated using the a_3 constants of Kuchitsu and Morino (1965): $a_3(\text{C-H})=1.981 \text{ Å}^{-1}$,
 $a_3(\text{N-H})=2.19 \text{ Å}^{-1}$.

^cThe f_{1111} values are calculated using the a_4 constants of Kuchitsu and Morino (1965): $a_4(\text{C-H})=2.087 \text{ Å}^{-1}$,
 $a_4(\text{N-H})=2.28 \text{ Å}^{-1}$.

The C-H and N-H equilibrium bond lengths used in the potential function expansions are presented in Table 24. The $\tilde{X}^1A'$ state bond lengths of HCN and of CNH are from the *ab initio* work of Pearson, Schaefer, and Wahlgren [1975]. The $\tilde{A}^1A''$ C-N bond length of HCN is from the empirical work of Bunker and Stone [1972] while that for CNH is from the *ab initio* work of Laidig and Schaefer [1983].

TABLE 24			
HCN/CNH C-H and N-H Equilibrium Bond Lengths.			
Molecule		State	
		$\tilde{X}A'$	$\tilde{A}A''$
$r_{CH} / \text{\AA}$	HCN	1.066	1.140
$r_{NH} / \text{\AA}$	CNH	0.9955	1.036

With the potential functions thus specified the Schrödinger equation was solved by Numerov-Cooley numerical integration on 500 points between the bond limits of 0.3 Å and 2.3 Å (which were chosen so as to guarantee that the potential function at these limits was at least ten times larger than the largest eigenvalue of interest). The calcu-

lated stretching energies are presented in Table 25 along with several observed energies and energies calculated with the semirigid bender model (taken from Tables 12 and 13). For the $\tilde{X}$ 'A' ground state of HCN and CNH the observed values are taken from Tables I and IV respectively. For the $\tilde{A}$ 'A' excited state the observed value for HCN is from Bunker and Stone [1972] while the N-H stretching vibration has not, of course, been seen in the $\tilde{A}$ 'A' state of CNH.

The agreement between the observed and calculated values is not as good as was the case for the ν_1 vibration. This is mainly due to the very large amplitude of the "H" stretching vibration which therefore explores a much larger part of its potential function than does the C-N stretching vibration. As a result any inadequacies in the approximated potential function for the "H" stretching vibration have a much greater impact on the calculated energies than they do for the C-N stretching vibration. The calculated energies are, however, well within 10% of the observed values and as the "H" stretching Franck-Condon factors are only being calculated to investigate the non-appearance of the ν_1 levels in the electronic spectrum, this agreement is satisfactory.

The calculated absorption and emission Franck-Condon factors for the "H" stretching vibrations are given in Table 26 and 27, respectively. It is immediately seen that these Franck-Condon factors decrease very quickly with increasing Δv_1 , explaining the absence of this vibration in the emis-

TABLE 25

HCN/CNH "H" Stretching Frequencies: Observed and
Calculated (cm^{-1}).^a

State	Molecule	v_1	obs ^a	SRB ^b	Anh ^c
$\bar{X}A'$	HCN	0	0	0	0
		1	3311	3308	3337
		2	6520	6518	6627
		3	9627	9629	9921
		4	12636	12641	13256
	CNH	0	0	0	0
		1	3653	3665	3692
		2		6706	7329
		3			10975
		4			14674
$\bar{X}A''$	HCN	0	0		0
		1	3123		3031
		2			6023
		3			9029
		4			12086
	CNH	0			0
		1			3172
		2			6305
		3			9465
		4			12695

^aSee text for the sources of these values.

^bCalculated using the SemiRigid Bender model as described in Chapter II.

^cCalculated using the Numerov-Cooley technique and the anharmonic potential functions as described in the text. These values are very inaccurate and are only included for illustrative purposes.

sion spectrum of Baronavski [1979] and the fact that only one transition involving $v_1 \neq 0$ is seen in the absorption spectrum (Bunker and Stone [1972]). In the case of the absorption spectrum Herzberg and Innes [1957] point out that the upper $v_1 = 1$ state may be predissociated to some extent. This would further decrease the apparent intensity of any transitions to the $v_1 = 1$ state as such transitions would be somewhat broadened. As the Franck-Condon factors for the N-H stretching vibration of CNH decrease even faster than those for HCN it is not likely that this vibration will be found in the electronic spectrum of this molecule.

TABLE 26

HCN/CNH "H" Stretching Vibration:
Franck-Condon Absorption Factors.

Transition $v_1'' = 0, v_1'$	$ \langle v_1'' v_1' \rangle ^2$	
	HCN	CNH
0	.777	.915
1	.177	.080
2	.036	.004
3	.008	
4	.002	
Total ^a	1.000	.999

^aThis total represents the fraction of the total intensity accounted for by the transitions included in the sum.

TABLE 27

HCN/CNH "H" Stretching Vibration:
Franck-Condon Emission Factors.

Transition $v_1' = 0, v_1''$	$ \langle v_1' v_1'' \rangle ^2$	
	HCN	CNH
0	.777	.915
1	.210	.081
2	.012	.003
Total ^a	.999	.999

^aThis total represents the fraction of the total intensity accounted for by the transitions included in the sum.

4.2 ABSORPTION

The infrared (vibrational) and ultraviolet (electronic) absorption spectra of HCN are well known. For CNH, however, only a few vibrational levels have been seen and the $\tilde{A}$ - $\tilde{X}$ electronic absorption system has yet to be identified. To perhaps aid in its eventual identification the semirigid bander wavefunctions were used to calculate relative intensities for both the HCN and CNH conformations. By comparing the calculated HCN intensities with those observed experi-

mentally by Herzberg and Innes [1957] it is then possible to gauge the reliability of the present model and thus the reliability of the calculated CNH intensities.

The intensity for absorption from the ground state rotation-bending level $|rb''\rangle$ (ψ_b^K of Eq. 11) to the excited state level $|rb'\rangle$, was calculated by the formula,

$$I = \nu |\langle rb' | M_C(\rho) | rb'' \rangle|^2 e^{-E/KT} \quad (37)$$

where the temperature was taken as 22°C and the effects of the stretching vibrations are not included. (See Table 21, above, for the Franck-Condon factors for absorption for the C-N stretching vibration). This formula represents the energy intensity of the absorption rather than the photon number intensity. This seemed the more reasonable choice for comparison with the experimental intensities which are roughly estimated from the photographic density of the absorption bands. Such "eyeballed" relative intensities are only expected to be good to perhaps an order of magnitude when an entire set is considered at once (Huber [1983]).

4.2.1 HCN

Herzberg and Innes [1957] observed ultraviolet absorption from the four lowest lying vibrational levels of the $\tilde{X}^1A'$ ground state of HCN to many levels of the $\tilde{A}^1A''$ excited state. In their work they present roughly estimated rela-

tive band intensities for these transitions. Based on exposures taken with a wide range of HCN pressures they assigned relative intensities ranging from 0.5 to over 5000. These intensities were estimated from the relative darkening of the photographic plates and are thus rather uncertain.

By using the semirigid bender wavefunctions for the $\tilde{X}$ 'A' ground and the $\tilde{A}$ 'A' excited electronic states, in the formula given above, relative intensities were calculated for absorption from the same four lowest lying vibrational levels of the ground state to *non-stretching levels* of the upper state. These calculated relative intensities are presented in Table 28 along with the intensities reported by Herzberg and Innes [1957]. In this table it can be seen that the general trends of the calculated values seem to agree fairly well with the experimental ones. (The fact that these values are of the same order of magnitude is entirely coincidental - both intensity scales are in completely arbitrary units).

To examine this agreement in more detail a log-log plot of the calculated versus observed intensities is given in Fig. 16. In principle, if both intensity scales corresponded precisely to the same physical quantity, the points on this graph should fall on a line of unit slope (but arbitrary intercept). The actual best-fit line is shown in Fig. 16 by the solid line while the best-fit line of unit slope is shown by the long-dashed line. The ninety-five percent

TABLE 28
HCN Calculated Absorption Intensities.

Ground State	Excited State	Intensity obs	Intensity calc	Excited State	Intensity obs	Intensity calc
(0,0 ⁰ ,0) E=0.0 cm ⁻¹ B=1.00 ^b	(0,0,0) ¹	5 ^a	11			
	(0,1,0) ¹	25	78			
	(0,2,0) ¹	120	306			
	(0,3,0) ¹	350	839			
	(0,4,0) ¹	1000	1732			
	(0,5,0) ¹	3000	2728			
	(0,6,0) ¹	4000 ^c	3134			
	(0,7,0) ¹	4000	2435			
	(0,8,0) ¹	3000	1243			
	(0,9,0) ¹		446			
(0,1 ¹ ,0) E=713 cm ⁻¹ B=0.0309	(0,0,0) ⁰	1	2.7	(0,0,0) ²	1	2.4
	(0,1,0) ⁰	6	16	(0,1,0) ²	6	14
	(0,2,0) ⁰	15	51	(0,2,0) ²	18	44
	(0,3,0) ⁰	30	112	(0,3,0) ²	35	93
	(0,4,0) ⁰	50	179	(0,4,0) ²	150	147
	(0,5,0) ⁰	150	208	(0,5,0) ²	200	172
	(0,6,0) ⁰	150	155	(0,6,0) ²	150	151
	(0,7,0) ⁰		44	(0,7,0) ²		97
	(0,8,0) ⁰		0.026	(0,8,0) ²		47
	(0,9,0) ⁰		6.5	(0,9,0) ²		18
(0,2 ⁰ ,0) E=1411 cm ⁻¹ B=0.00103	(0,0,0) ¹		0.59			
	(0,1,0) ¹	0.5	2.7			
	(0,2,0) ¹	1	6.3			
	(0,3,0) ¹	2	9.5			
	(0,4,0) ¹	6	9.5			
	(0,5,0) ¹		5.6			
	(0,6,0) ¹		1.3			
	(0,7,0) ¹		0.019			
	(0,8,0) ¹		0.74			
	(0,9,0) ¹		0.91			

$(0,2^2,0)$	$(0,0,0)^1$	0.35	$(0,0,0)^3$	0.28
$E=1427 \text{ cm}^{-1}$	$(0,1,0)^1$	1.7	$(0,1,0)^3$	1.4
$B=0.000949$	$(0,2,0)^1$	4.3	$(0,2,0)^3$	3.5
	$(0,3,0)^1$	7.4	$(0,3,0)^3$	5.9
	$(0,4,0)^1$	8.9	$(0,4,0)^3$	7.4
	$(0,5,0)^1$	7.5	$(0,5,0)^3$	7.1
	$(0,6,0)^1$	3.9	$(0,6,0)^3$	5.2
	$(0,7,0)^1$	0.93	$(0,7,0)^3$	3.0
	$(0,8,0)^1$	0.029	$(0,8,0)^3$	1.4
	$(0,9,0)^1$	0.039	$(0,9,0)^3$	0.51

^aThe observed intensities are taken from Herzberg and Innes (1957).

^bThe "B" values are the Boltzmann factors evaluated at 22°C.

confidence interval (for single measurement uncertainties, not averages) is shown by the short-dashed lines. It can be seen that all of the points on the graph fall within this confidence interval.

The agreement is satisfactory and indicates that the relative intensities for CNH that are calculated in the next section should be reliable.

4.2.2 CNH

The $\tilde{A}$ 'A' first excited electronic state of CNH has not yet been seen. This fact formed part of the motivation for performing the intensity calculations presented in this work.

One experiment that has recently been done (Huber [1983]) was motivated by the observation of infrared absorption bands of CNH in hot HCN by Maki and Sams [1981]. This observation raised the possibility of observing the $\tilde{A}-\tilde{X}$ electronic absorption spectrum of CNH in hot HCN. With the *ab initio* calculation of Laidig and Schaefer [1983] for the $\tilde{A}$ 'A' state of CNH it became clear that the potential minimum for the excited state of CNH lies about 5000 cm^{-1} below that of HCN, the opposite to the situation in the ground state (see Fig. 42). In particular this meant that the origin of the $\tilde{A}-\tilde{X}$ system of CNH should fall about 10000 cm^{-1} to the red of the origin of the $\tilde{A}-\tilde{X}$ system of HCN and thus be easier to identify than if this were not the case. However, as was discussed above, the calculated Franck-Condon factors for absorption for the C-N stretching vibration of CNH only reach their maximum at a value of $v'_2 \geq 9$ (see Table 21). For upper state C-N stretching levels lower than about $v'_2 = 6$ the Franck-Condon factors become very small. This has the implication that the strongest part of the CNH $\tilde{A}-\tilde{X}$ absorption system could lie 10000 cm^{-1} to the blue of the system origin and thus may lie *underneath* the strong $\tilde{A}-\tilde{X}$ absorption system of HCN for which the Franck-Condon factors are already large at $v'_2 = 0$, or 1. This may partially explain the lack of success to date in identifying CNH in the ultraviolet absorption spectrum of hot HCN (Huber [1983]).

The calculated transition intensities for absorption from the four lowest lying vibrational levels of the A' ground state of CNH are given in Table 29. These were calculated in the same manner as was used for the HCN absorption intensities and do *not* include the C-N stretch Franck-Condon factors (which are given in Table 21). The general trends and magnitudes of these calculated intensities are similar to those of HCN and, based on the level of agreement which was obtained between the observed and calculated intensities for HCN, these results should be reasonably reliable.

As the ground state vibrational spacings in CNH are significantly smaller than those in HCN the Boltzmann factors for the hot bands of CNH are correspondingly larger. In particular the strongest transition in the ν_2 hot band of CNH is only five times weaker than the fundamental, instead of fifteen times weaker as is the case for HCN. For the $2\nu_2$ hot bands these factors are forty times weaker for CNH, as opposed to over 300 times weaker for HCN.

The general conclusion of this section is thus that the CNH $\tilde{A}-\tilde{X}$ absorption spectrum will probably have its maximum intensity at very high overtones of the C-N stretching vibration in the upper state. This part of the spectrum will lie near or under the strong $\tilde{A}-\tilde{X}$ system of HCN and therefore may be difficult to identify. If it is eventually identified the hot bands will be significantly more important than they are for HCN.

TABLE 29
CNH Calculated Absorption Intensities.

Ground State	Excited State	Intensity	Excited State	Intensity
(0,0 ⁰ ,0) E=0.0 cm ⁻¹ B=1.00 ^a	(0,0,0) ¹	124		
	(0,1,0) ¹	597		
	(0,2,0) ¹	1819		
	(0,3,0) ¹	4013		
	(0,4,0) ¹	5806		
	(0,5,0) ¹	4048		
	(0,6,0) ¹	1056		
	(0,7,0) ¹	119		
	(0,8,0) ¹	7.1		
	(0,9,0) ¹	0.25		
(0,1 ¹ ,0) E=464 cm ⁻¹ B=0.104	(0,0,0) ⁰	85	(0,0,0) ²	81
	(0,1,0) ⁰	308	(0,1,0) ²	288
	(0,2,0) ⁰	699	(0,2,0) ²	637
	(0,3,0) ⁰	1092	(0,3,0) ²	961
	(0,4,0) ⁰	986	(0,4,0) ²	907
	(0,5,0) ⁰	190	(0,5,0) ²	455
	(0,6,0) ⁰	22	(0,6,0) ²	109
	(0,7,0) ⁰	37	(0,7,0) ²	14
	(0,8,0) ⁰	7.3	(0,8,0) ²	0.96
	(0,9,0) ⁰	0.63	(0,9,0) ²	0.045
(0,2 ⁰ ,0) E=932 cm ⁻¹ B=0.0106	(0,0,0) ¹	46		
	(0,1,0) ¹	108		
	(0,2,0) ¹	152		
	(0,3,0) ¹	117		
	(0,4,0) ¹	26		
	(0,5,0) ¹	3.3		
	(0,6,0) ¹	18		
	(0,7,0) ¹	7.6		
	(0,8,0) ¹	1.3		
	(0,9,0) ¹	0.11		

$(0,2^2,0)$	$(0,0,0)^1$	29	$(0,0,0)^3$	27
$E=946 \text{ cm}^{-1}$	$(0,1,0)^1$	76	$(0,1,0)^3$	69
$B=0.00991$	$(0,2,0)^1$	128	$(0,2,0)^3$	114
	$(0,3,0)^1$	139	$(0,3,0)^3$	126
	$(0,4,0)^1$	78	$(0,4,0)^3$	87
	$(0,5,0)^1$	11	$(0,5,0)^3$	35
	$(0,6,0)^1$	0.32	$(0,6,0)^3$	7.7
	$(0,7,0)^1$	1.2	$(0,7,0)^3$	1.0
	$(0,8,0)^1$	0.33	$(0,8,0)^3$	0.076
	$(0,9,0)^1$	0.034	$(0,9,0)^3$	0.0048

^aThe "B" values are the Boltzmann factors evaluated at 22°C.

4.3 EMISSION

Baronovski [1979] has observed laser induced fluorescence (LIF) from two of the lowest lying vibrational levels ($(0,0,0)^0$ and $(0,1,0)^1$) of the $\tilde{A}^1A'$ first excited state of HCN. The dispersed fluorescence was recorded, at very low resolution (about 5 Å which, in the region of the spectrum, 1900-2800 Å, corresponds to approximately $\pm 100 \text{ cm}^{-1}$) with a photomultiplier. As a photomultiplier is basically a photon counting device the intensities that were calculated for emission from the excited state stretching-bending-rotating levels $|srb'\rangle$ to the ground state levels $|srb''\rangle$ were determined in terms of photon number intensity by the formula,

$$\begin{aligned}
 I &= \nu^2 |\langle srb' | M_c(\rho) | srb'' \rangle|^2, \\
 &= \nu^2 |\langle rb' | M_c(\rho) | rb'' \rangle|^2 |\langle s' | s'' \rangle|^2.
 \end{aligned}
 \tag{38}$$

The rotation-bending overlaps were calculated as described at the beginning of this chapter while the stretching Franck-Condon factors are taken from Table 22.

The calculated intensities were convoluted with a Lorentzian lineshape of 5 Å width to generate simulated spectra directly comparable to the experimental spectra. Five Angstroms was chosen as the linewidth after initial calculations using the resolution calculated by Baronavski [1979] (2.5 to 3 Å) as the linewidth, indicated that significantly more detail should have been observed with such a resolution.

As the calculated intensities were *not* convoluted with an instrument response profile it is expected that the relative scales between the observed and calculated spectra will *not* be uniform across the range of these spectra. However, as the instrument response profile is most likely a slowly varying function, the relative scaling between closely neighbouring peaks on the two spectra is expected to be reasonably constant.

The goal of the study of the HCN/CNH emission was to calculate simulated spectra for the two observed HCN fluorescence spectra, and, if the agreement between observed and calculated was satisfactory, equivalent spectra for CNH would then be calculated as predictions. This goal was only partially achieved due to problems with the HCN $\tilde{A}^1A''(0,1,0)^+$ fluorescence spectrum, for which a predicted

spectrum for CNH was therefore *not* calculated. For the $\tilde{A} \text{ } ^1A''(0,0,0)^\circ$ fluorescence spectrum, however, the observed and calculated spectra for HCN were in good agreement and thus a simulated spectrum for CNH *was* calculated and is believed to be reasonably reliable.

4.3.1 HCN

4.3.1.1 $\tilde{A} \text{ } ^1A''(0,0,0)^\circ$ Spectrum.

Baronavski [1979] obtained the $\tilde{A} \text{ } ^1A''(0,0,0)^\circ$ fluorescence spectrum by laser excitation of the $\tilde{A} \text{ } ^1A''(0,0,0)^\circ - \tilde{X} \text{ } ^1A'(0,1^1,0)$ transition at 1940 Å. Fig. 17 shows both the calculated (solid curve) and observed (dotted curve - from Baronavski [1979]) spectra for emission from — the $(0,0,0)^\circ$ level of the $\tilde{A} \text{ } ^1A''$ excited state of HCN. In this figure the transitions are labelled by the ground state vibrational quantum numbers.

The agreement between the observed and calculated spectra can be seen to be very good. In particular, both the observed positions, and the observed relative intensities of neighbouring peaks, are well reproduced in the calculated spectrum. The relative intensity scale across the full wavelength range, however, is not equivalent in the two spectra. This was not unexpected, as was mentioned above, and can be attributed to the unknown response function of the instrument which recorded the observed spectrum. (And also to any imprecision in the calculated Franck-Condon factors.)

The excellent agreement between the observed and calculated $\tilde{A} A''(0,0,0)^0$ emission spectra indicates that the calculated $\tilde{A} A''(0,0,0)^0$ emission spectrum for CNH should be quite reliable.

4.3.1.2 $\tilde{A} A''(0,1,0)^1$ Spectrum.

Fig. 18 shows the calculated (upper curve) and observed (lower curve - from Baronavski [1979]) $\tilde{A} A''(0,1,0)^1$ emission spectrum for HCN. Unlike the $\tilde{A} A''(0,0,0)^0$ spectrum

the agreement here is *not* good at all. The relative intensities of neighbouring peaks in the two spectra do *not* agree and some of the experimentally observed peaks appear to be almost entirely missing in the calculated spectrum. These "missing" peaks are indicated in Fig. 18 by the black shading.

To examine this problem in greater detail, intensities for the $\tilde{A}^1A''(0,1,0)^1$ emission spectrum were calculated for optimized $\tilde{A}^1A''$ state potential functions determined with bond angles different from the 120.9° (Bunker and Stone [1972]) that was used in Chapter III. This involved a new least squares fitting of the excited state for each of the different HCN bond angles considered, following which the $\tilde{A}^1A''(0,1,0)^1$ wavefunction was used to calculate bending overlaps which were then used to calculate intensities and the simulated emission spectrum. This was done for $\alpha_e = 118^\circ, 120^\circ, 122^\circ$, and 124° , and the simulated spectra that were thus calculated are shown by the curves in Fig. 19. Baronavski's [1979] observed spectrum is again indicated by the lower curve and the missing peaks are shown by the black shading.

There are two main features to note from Fig. 19.

1. First, that the relative intensities of neighbouring peaks are in good agreement with the observed spectrum in *none* of these calculated spectrum.

This point is discussed further before moving on to the second point.

The $\tilde{A}^1A''(0,1,0)$ emission spectrum consists mainly of a long progression in the ground state C-N stretching vibration ν_1 . This progression is built upon a short progression in the ν_2 bending vibration with the most intense part generally involving $\nu_2'' = 10^\circ, 12^\circ$, and 14° . In Fig. 19 those peaks whose transitions share a common stretching level in the ground state are shaded in the same way. The transitions with the same shading therefore all involve the same C-N stretching transition, and therefore have the same Franck-Condon factor for the C-N stretching part of the intensity. The problem can thus be clearly seen in Fig. 19. The observed intensities are spread more evenly over $\nu_2'' = 10^\circ, 12^\circ$, and 14° than are the calculated intensities. By forcing the upper state to be more bent (α_e smaller), more intensity, as would be expected, was added to the $\nu_2'' = 14^\circ$ transitions, but only at the expense of making the $\nu_2'' = 10^\circ$ transitions much weaker. Forcing the upper state to be more linear has the reverse effect. As the Franck-Condon factors for the similarly shaded peaks are the same it is only the bending part of the intensity calculation that could be involved in explaining this discrepancy.

2. The second, and perhaps more important, point to note about Fig. 19 is that there are several peaks which, though seen strongly in the observed spectrum, do not

show up with significant intensity in *any* of the calculated spectra. These "missing" peaks are indicated in this figure by the black shading and are connected by vertical lines.

As inaccuracies in the calculated stretching overlaps would not be sufficient to explain this point - the Franck-Condon factors used here are the same as those used for the $\tilde{A}^1A''(0,0,0)^\circ$ spectrum which did not have such problems - and cannot explain the first point - in which the stretching contribution was "factored out" - then either the bending part of the model is poor, or the experimental results are not as straightforward as they appear. (Or some combination of these two possibilities could be true.)

With regard to the first possibility, the weakest point of the model is clearly the unknown form of the transition moment and until *ab initio* results are available there is not a great deal that can be done in this area. The fact that the choices $M_C(\rho) = \tau$, and $\sin \tau$ had little effect on the calculated relative emission intensities would seem to indicate that for this to be a good explanation of the discrepancy in intensities $M_C(\rho)$ must have a rather more complicated behaviour. This does, however, seem the likeliest explanation of the first point and may indicate that a fitting of the transition moment to the observed intensities could be done, but until a better experimental spectrum is available this would probably not be worthwhile.

The second weakest point of the model is the lack of a clearly reliable geometry for the excited state. The best current value for α_e is presumably the 120.9° of Bunker and Stone [1972] but this value was *not* obtained by a proper least squares fitting and is significantly different from the value of 125° obtained by Herzberg and Innes [1957]. *Ab initio* values range from 127.8° (Ditchfield *et. al.* [1972]) and 127.2° (Schwenzer *et. al.* [1974]) to the more recent value of 122.8° (Laidig and Schaefer [1983]) and are thus of little help in resolving the issue.

(An important ongoing project is the addition of rotation to the current semirigid bender model, so as to allow the least squares fitting to the vibration *rotation* levels of HCN/CNH and thus to allow the determination of a reliable geometry for the excited state.)

With regard to any ambiguity in the experimental spectra it must be emphasized that Baronavski's [1979] spectra can best be characterized as weak, overlapped, and poorly resolved. More important, the relatively broad bandwidth of the exciting laser admits the possibility that more than one upper state level may have been populated. This possibility is next discussed in detail.

Baronavski's $\tilde{A}^1A''(0,1,0)^1$ emission spectrum was observed by exciting HCN with a pulsed ArF laser tuned to $1931 \text{ \AA}$ and operating with a line width of $0.3 \text{ \AA}$. The $\tilde{A}^1A''(0,1,0)^1 \rightarrow \tilde{X}^1A'(0,2^*,0)$ transition, with origin at

1930.0 Å, lies in this region and is responsible for populating the $\tilde{A} \text{ } ^1A''(0,1,0)^1$ level. The only other transition nearby that involves a ground state level with energy less than 2500 cm^{-1} , is $\tilde{A} \text{ } ^1A''(0,0,1)^2 - \tilde{X} \text{ } ^1A'(0,3^1,0)$, with origin at 1932.8 Å. Due to the smaller effective $\bar{B}$ value in the $\tilde{A} \text{ } ^1A''$ excited state than in the $\tilde{X} \text{ } ^1A'$ ground state, the R branches of the $\tilde{A} - \tilde{X}$ transition only extend a short distance to the blue before reaching a head. This head is generally about 0.3-0.5 Å to the blue of the band origin and thus for the $\tilde{A} \text{ } ^1A''(0,0,1)^2 - \tilde{X} \text{ } ^1A'(0,3^1,0)$ transition lies at about 1932.3-1932.5 Å. This is still somewhat distant from the laser at 1931 Å but it is not clear how accurate the laser tuning is, nor how certain is the claimed linewidth of 0.3 Å.

Assuming that the two transitions were excited by the laser, could the $\tilde{A} \text{ } ^1A''(0,0,1)^2$ level have significant population relative to the $\tilde{A} \text{ } ^1A''(0,1,0)^1$ level? The three factors which must be considered in determining the resultant relative populations of the excited state levels, are the relative populations of the involved ground states (determined by the Boltzmann factors), and the stretching and bending contributions to the intensity of absorption from each of the involved ground states. Each of these factors is considered in turn below.

1. The ground state $\tilde{X} \text{ } ^1A'(0,3^1,0)^1$ level of the $\tilde{A} \text{ } ^1A''(0,0,1)^2 - \tilde{X} \text{ } ^1A'(0,3^1,0)$ transition, which could

populate the $\tilde{A}^1A''(0,0,1)^1$ level, lies at 2111 cm^{-1} and therefore at room temperature has a population about $1/31$ that of the $\tilde{X}^1A'(0,2^0,0)$ level which lies at 1409 cm^{-1} and which is responsible for populating the $\tilde{A}^1A''(0,1,0)^1$ level.

2. This much reduced ground state population is somewhat offset by the Franck-Condon factors for absorption for the C-N stretching vibration. From Table 21 it can be seen that the $\nu_1(1-0)$ transition involved in populating the $\tilde{A}^1A''(0,0,1)^1$ level is expected to be roughly 3.1 times stronger than the $\nu_1(0-0)$ transition involved in populating the $\tilde{A}^1A''(0,1,0)^1$ level.
3. Finally, the contribution of the bending overlaps to the absorption intensity of these two transitions was determined, on the basis of the semirigid bender wavefunctions, and it was found that the transition leading to the $\tilde{A}^1A''(0,1,0)^1$ level was favoured by a factor of 1.2. (As the upper state constants and wavefunctions are not corrected for the effects of stretching averaging the $\tilde{A}^1A''(0,0,1)^1$ - $\tilde{X}^1A'(0,3^1,0)$ bending overlap was approximated by using the $\tilde{A}^1A''(0,0,0)^1$ - $\tilde{X}^1A'(0,3^1,0)$ bending overlap. As experience has shown that the bending overlaps only change slowly with ν_1 , this approximation is of minor importance.)

Combining these three factors the relative populations of the excited states, assuming that both were indeed excited by the laser, are found to be,

$$\begin{aligned} \text{Pop}[\tilde{A}^1A''(0,1,0)] & \\ &= (31 \times 1.2 / 3.1) \text{Pop}[\tilde{A}^1A''(0,0,1)] \\ &= 12 \text{Pop}[\tilde{A}^1A''(0,0,1)]. \end{aligned} \quad (39)$$

The reliability of this factor is difficult to estimate as the actual populations will depend on detailed effects in the interaction of the laser and the gas. One factor of importance is that the $\tilde{A}^1A''$ state of HCN is subject to pre-dissociation. In particular, the fluorescence lifetimes (which are a measure of all state quenching effects) of the vibrational levels in the $\tilde{A}^1A''$ state of HCN have been seen to vary dramatically, for example, with K (Wallace [1983]). Thus it is possible that the emission from the $\tilde{A}^1A''(0,0,1)$ level could be enhanced relative to that from the $\tilde{A}^1A''(0,1,0)$ level if the latter were quenched more rapidly by dissociation or some other process. The important point, however, is that if both of these transitions are excited by the laser, the resulting population of the $\tilde{A}^1A''(0,0,1)$ level might not be insignificant.

With this established, the simulated spectrum for emission from the $\tilde{A}^1A''(0,0,1)$ level was calculated and is shown in Fig. 20 along with observed (Baronovski [1979]) and

calculated $\tilde{A}^1A''(0,1,0)^1$ (from Fig. 18) spectra. In this figure the two calculated spectra are drawn with the same relative intensity scale.

From Fig. 20 it is immediately apparent that the "missing" peaks in the calculated $\tilde{A}^1A''(0,1,0)^1$ spectrum, which are again indicated by the black shading and are connected by the solid vertical lines, are found to have quite significant intensity in the calculated $\tilde{A}^1A''(0,0,1)^2$ spectrum. In particular the three indicated "missing" peaks are 8.2, 12.1, and 7.3 times stronger in the calculated emission for the $\tilde{A}^1A''(0,0,1)^2$ level than in the emission calculated for the $\tilde{A}^1A''(0,1,0)^1$ level. These factors are indicated in Fig. 20. As the population of the $\tilde{A}^1A''(0,0,1)^2$ level was roughly estimated as being about 1/12 that of the $\tilde{A}^1A''(0,1,0)^1$ level (Eq. 39), it is not unreasonable to suppose that some contribution to the "missing" peaks may indeed come from emission from the $\tilde{A}^1A''(0,0,1)^2$ level.

Thus the conclusion is that the $\tilde{A}^1A''(0,1,0)^1$ HCN emission spectrum observed by Baronavski [1979] may, in part, consist of the $\tilde{A}^1A''(0,0,1)^2$ emission spectrum. The problems that were encountered with the bending overlaps are probably due to some combination of the crude approximation used for the transition moment function, and the uncertainty of the geometry of the $\tilde{A}^1A''$ excited state. A repetition of the fluorescence experiment, but with better resolution and, more important, a more finely tuned excitation source, would

Figure 20: The Calculated HCN $\tilde{A}A''(0,0,1)^2$ Fluorescence Spectrum.

go far in clearing up some of the confusion remaining in this spectrum.

As a final point about this spectrum, it is interesting to note that Baronavski [1979] says that the fluorescence observed when the laser was operating in broadband mode (12 Å) over the region between the two transitions, $\tilde{A}^1A''(0,1,0)^1 - \tilde{X}^1A'(0,2^0,0)$ and $\tilde{A}^1A''(0,0,0)^0 - \tilde{X}^1A'(0,1^1,0)$, was merely the sum of the $\tilde{A}^1A''(0,1,0)^1$ and $\tilde{A}^1A''(0,0,0)^0$ emission spectra. Such an experiment, however, must surely populate both the $\tilde{A}^1A''(0,0,1)^2$ level as discussed above, and also, by the $\tilde{A}^1A''(0,0,0)^2 - \tilde{X}^1A'(0,1^1,0)$ transition at 1936.8 Å, the $\tilde{A}^1A''(0,0,0)^2$ level. That new peaks do *not* appear in the broadband mode spectrum is somewhat puzzling and suggests that perhaps some of the emission peaks from these two upper state levels may already appear in one or the other of the $\tilde{A}^1A''(0,1,0)^1$ and $\tilde{A}^1A''(0,0,0)^0$ spectra.

One also wonders why the fluorescence spectrum for the $\tilde{A}^1A''(0,0,0)^2 - \tilde{X}^1A'(0,1,0)^1$ excitation was not recorded (by Baronavski, or, if it was, why it isn't mentioned. This excitation produced a fluorescence excitation signal about five times stronger than the $\tilde{A}^1A''(0,0,0)^0 - \tilde{X}^1A'(0,1,0)^1$ excitation (see Fig. 4 of Baronavski [1979]), due to the much greater laser power available at this wavelength.

With all of this confusion surrounding the $\tilde{A}^1A''(0,1,0)^1$ emission spectrum, why then was the $\tilde{A}^1A''(0,0,0)^0$ spectrum so straightforward? The answer appears to lie in the fact

that there are no other excitations lying very close to the exciting laser at 1940 Å, the nearest being the $\tilde{A}^1A''(0,0,0) \rightarrow \tilde{X}^1A'(0,1,0)$ transition at 1936.2 Å which was mentioned above.

4.3.2 CNH

4.3.2.1 $\tilde{A}^1A''(0,0,0)^\circ$ Spectrum.

The calculated spectra for CNH emission from the $\tilde{A}^1A''(0,0,0)^\circ$ level is shown in Fig. 21. Due to the uncertainty in the *ab initio* value for the energy of the potential minimum in the $\tilde{A}^1A''$ excited state, this spectrum could be shifted to the red or blue by about 2000 cm^{-1} (Laidig and Schaefer [1983]) or, in this region, about 100 Å. The spacing between the peaks is also subject to an undetermined error due to the uncertainty in the *ab initio* value for $f_{\alpha\alpha}$ and also due to the extended extrapolation beyond known, or reliably calculated, energy levels, that was involved in calculating this spectrum.

The calculated spectrum consists of a long and dilute progression in the ν_1 C-N stretching vibration, which peaks at $\nu_1 \geq 9$. This progression is built on a short bending progression involving mainly $\nu_2'' = 2^\circ, 4^\circ$, and 6° . The peaks are labelled in Fig. 21 according to their ground state vibrational quantum numbers and this spectrum was calculated in the same manner as was the HCN $\tilde{A}^1A''(0,0,0)^\circ$ spectrum.

The $\tilde{A}' A''(0,0,0)^0$ level of CNH would, however, be rather difficult to populate by excitation from the $\tilde{X}' A'$ ground state due to the very small Franck-Condon factor for the $v_2(0-0)$ transition.

Chapter V

OTHER MOLECULES

There are many candidate triatomic molecules for internal rotation and the present computer program is eminently suited to consider the molecular ions $\text{HCO}^+/\text{COH}^+$ and $\text{HNN}^+/\text{NNH}^+$, which are iso-electronic with HCN/CNH . The bending vibration structure of these ions has not yet been observed experimentally. The calculations reported here thus rely entirely on *ab initio* results.

5.1 $\text{HOC}^+/\text{HCO}^+$

As no experimental data are available for the bending energy levels of $\text{HCO}^+/\text{COH}^+$ it is not possible to do a least squares fitting of the parameters of the potential function. Instead, by using the *ab initio* data of Hennig, Kraemer, and Diercksen [1977], Nobes and Radom [1981], and Kraemer and Bunker [1983], a "straight-through" calculation of bending energy levels was done.

For this calculation the bond length functions were parameterized by seven parameters. Four of these parameters are the bond lengths at the linear equilibrium configurations of each isomer,

$$\begin{aligned} r_{\text{Ha}}(\text{HCO}^+) &= r_{\text{Ha}}(\tau = 0), & r_{\text{Ha}}(\text{COH}^+) &= r_{\text{Ha}}(\tau = \pi), \\ r_{\text{Co}}(\text{HCO}^+) &= r_{\text{Co}}(\tau = 0), & r_{\text{Co}}(\text{COH}^+) &= r_{\text{Co}}(\tau = \pi). \end{aligned}$$

Another parameter used is the bending angle corresponding to the position of the barrier,

$$\tau_0,$$

and the remaining two parameters are the bond lengths at the "Transition State" (TS),

$$r_{\text{Ha}}(\tau_0),$$

$$r_{\text{CO}}(\tau_0).$$

This parameterization was chosen on the basis of the available *ab initio* data. The values used for these parameters are presented in Table 30.

The bending potential function was parameterized exactly as was done in Chapter II for the $\tilde{X}$ 'A' ground state of HCN/CNH, with the minor exception that τ_0 is now being considered as a geometry parameter. The bending potential function parameters actually used in the semirigid bender calculation of the bending energy levels are given in Table 31 while the calculated bending energies are given in Table 32.

The bending energies given in Table 32 are presented in the order of the "total" bending quantum number (which is the number of nodes of the wavefunction between $\rho = 0$ and $\rho = \pi$) and thus in order of increasing energy when referred to a common zero. The energy values actually presented in this table are referred to the $(0,0^0,0)$ level of the relevant conformation (HCO⁺ or COH⁺). The zero point energies of the $(0,0^0,0)$ levels for these two conformations are also

TABLE 30

HCO⁺/COH⁺ Bond Length Parameters.as Fixed for Use in the Calculation
of the Bending Energy Levels.

Parameter	HCO ⁺ ^a	TS ^b	COH ⁺ ^b
$r_{\text{Ha}} / \text{\AA}$	1.725	1.211	1.483
$r_{\text{CO}} / \text{\AA}$	1.104	1.150	1.155

^aHCO⁺ values are from Hennig, Kraemer and Diercksen (1977).^bTransition State (TS) and COH⁺ values are from Nobes and Radom (1981).

included in the table and it should be remembered that the COH⁺ potential minimum was fixed at 13125 cm⁻¹ above that of HCO⁺.

Kraemer and Bunker [1983] have made an extensive *ab initio* study of the bending potential function of the COH⁺ ion. They then used their bending potential function in the conventional semirigid bender model to calculate some of the lower lying bending-rotational energy levels with, presumably, much greater precision than has been achieved here.

TABLE 31

HCO⁺/COH⁺ Bending Potential Function
Constants.

Parameter	HKD ^a	KB ^b	NR ^c
$f_{\alpha\alpha}(\text{HCO}^+)$ /aJ rad ⁻²	0.410		
$f_{\alpha\alpha}(\text{COH}^+)$ /aJ rad ⁻²		0.06491	
H_0 /cm ⁻¹			25663
τ_0 /degree			80.7
ΔE /cm ⁻¹			13125

^aFrom Hennig, Kraemer, and Dierksen (1977).^bFrom Kraemer and Bunker (1983).^cFrom Nobes and Radom (1981).

TABLE 32

HCO⁺/COH⁺ Bending Energies (cm⁻¹).

Total v ₂ (bent) ^a	HCO ⁺ Energy ^b	v ₂ ^l	COH ⁺ Energy ^{c,d}	v ₂ ^l
zero point energy	889		363	
0	0	0 ⁰		
1	1790	2 ⁰		
2	3572	4 ⁰		
3	5342	6 ⁰		
4	7097	8 ⁰		
5	8834	10 ⁰		
6	10549	12 ⁰		
7	12238	14 ⁰		
8			0	0 ⁰
9			733(749)	2 ⁰
10	13898	16 ⁰		
11			1491	4 ⁰
12			2296	6 ⁰
13	15523	18 ⁰		
14			3151	8 ⁰
15			4053	10 ⁰
16	17109	20 ⁰		
17			4994	12 ⁰
18			5967	14 ⁰
19	18648	22 ⁰		
20			6965	16 ⁰
21	20131	24 ⁰		
22			7979	18 ⁰
23	21546	26 ⁰		
24			8997	20 ⁰
25			10005	22 ⁰
26	22872	28 ⁰		
27			10982	24 ⁰
28	24063	30 ⁰		
29			11879	26 ⁰

^aThe "total" quantum number is the number of nodes of the wavefunction between $\rho=0$ and π .

^bMeasured from the $\text{HCO}^+(0,0^0,0)$ level.

^cMeasured from the $\text{COH}^+(0,0^0,0)$ level.

^dThe value in parentheses is from the more precise calculation of Kraemer and Bunker (1983).

The single pure bending energy level that they calculated is included in Table 32 for comparison and is in good agreement with the value obtained here.

Fig. 22 shows the bending potential function for $\text{HCO}^+/\text{COH}^+$. The horizontal lines represent the calculated energy levels. An important point to note from this figure is that the height of the barrier to internal rotation is calculated by Nobes and Radom [1981] to be significantly higher than the value calculated by Pearson *et al.* [1975] for HCN/CNH , and that the $\text{COH}^+-\text{HCO}^+$ energy difference is over two and a half times greater than the $\text{CNH}-\text{HCN}$ energy difference.

5.2 HNN⁺/NNH⁺

As was the case for the HCO⁺/COH⁺ ion, no experimental bending vibration data are available for HNN⁺/NNH⁺. In addition, *ab initio* calculations have only been done for the linear equilibrium configurations of this ion. As a result several approximations had to be made in choosing values for the semirigid bender model parameters. As HNN⁺ and NNH⁺ are equivalent, the properties of the molecule must be symmetric about $\tau = 90^\circ$. This of course greatly simplifies the choice of the parameters.

The parameterization used in the study of the ground state of HCN/CNH (Eqs. 17 and 18 and Fig. 4 in Chapter II) was chosen as the most appropriate for HNN⁺/NNH⁺. The available *ab initio* values are those of Hennig, Kraemer, and Diercksen [1977]. Their values for r_{Ha} , r_{NN} , and $f_{\alpha\alpha}$ were used in the present calculation. The remaining parameters (r_{Ha}'' , r_{NN}'' , and H_e) were estimated by noting that HCO⁺, HCN, and HNN⁺ form a natural sequence and appear to have similar characteristics (see, for example, Fig. 1 of Kraemer and Bunker [1983]). By following this sequence the barrier to internal rotation H_e was set at 15000 cm^{-1} ($H_e(\text{HCO}^+) = 25663 \text{ cm}^{-1}$, $H_e(\text{HCN}) = 17319 \text{ cm}^{-1}$). The second derivatives of the bond lengths were similarly estimated. r_{Ha}'' was set to $-0.969 \text{ \AA rad}^{-2}$ ($r_{\text{Ha}}''(\text{HCO}^+) = -0.968 \text{ \AA rad}^{-2}$, $r_{\text{Ha}}''(\text{HCN}) = -0.970 \text{ \AA rad}^{-2}$, where the HCO⁺ value is calculated from the

constants of Table 30). As $r_{\text{CO}}''(\text{HCO}^+)$ and $r_{\text{CN}}''(\text{HCN})$ are both rather small (0.076 and 0.049 Å rad⁻², respectively), and not consistent, it was decided to set $r_{\text{NN}}''(\text{HNN}^+) = 0.000$ Å rad⁻². This last approximation should have only a very slight effect on the calculated bending energies.

The parameter values, which were used for the calculation of the HNN⁺ energy levels, are given in Tables 33 and 34. The bending energies, bending spacings (ΔG), and the isomerization splittings, calculated with these parameters are given in Table 35 and are indicated by the horizontal lines in Fig. 23 which shows the bending potential function for HNN⁺/NNH⁺.

More than 2000 cm⁻¹ below the top of the potential barrier the isomerization splitting is quite small (less than 1 cm⁻¹). Higher than this, though, the isomerization splitting quickly becomes quite significant and above the barrier it soon becomes equal to the vibrational spacing (ΔG in Table 35). Once the splitting becomes apparent the bending levels are labelled with the "total" *bent convention* vibrational quantum number, which is the total number of nodes of the wavefunction, between $\rho = 0$ and π .

TABLE 33

HNN⁺/NNH⁺ Bond Length Parameters.

Parameter	HKD ^a	est ^b
$r_{\text{Ha}} / \text{\AA}$	1.5825	
$r_{\text{NN}} / \text{\AA}$	1.0968	
$r''_{\text{Ha}} / \text{\AA rad}^{-2}$		-0.969
$r''_{\text{NN}} / \text{\AA rad}^{-2}$		0.0

^aFrom Hennig, Kraemer, and Diercksen (1977).

^bEstimated, see text.

TABLE 34

HNN⁺/NNH⁺ Bending
Potential Function
Parameters.

Parameter	HKD ^a	est ^b
$f_{\alpha\alpha}(\text{HNN}^+)$ /aJ rad ⁻²	0.287	
H_0 /cm ⁻¹		15000

^aFrom Hennig, Kraemer, and
Diercksen (1977).

^bEstimated, see text.

TABLE 35

HNN⁺/NNH⁺ Bending Energies (cm⁻¹).

v_2^l	Energy	ΔG
0 ⁰	0	1507
2 ⁰	1507	1460
4 ⁰	2967	1413
6 ⁰	4380	1367
8 ⁰	5747	1318
10 ⁰	7065	1270
12 ⁰	8335	1218
14 ⁰	9553	1161
16 ⁰	10714	1097
18 ⁰	11811	1018
20 ^a	12829	3 ^b
21	12832	
22	13714	47
23	13761	
24	14363	283
25	14646	
26	15126	481
27	15607	
28	16133	567
29	16700	

882

602

480

526

^aThe quantum numbers for the rest of the table are the number of nodes of the entire wavefunction (from $\tau=0$ to $\tau=\pi$).^b

^bThe numbers given in this column are the isomerization splittings.

5.3 HIGH ENERGY LIMIT

It can be important, in some circumstances, to have some idea of the density of states of a molecule at high energy. This is particularly true in considering Raman intensities, vibrational dissociation, or in the calculation of various thermodynamic properties of a molecule, especially those involving the partition function. A standard treatment performed by considering harmonic oscillators is clearly inappropriate in the case of internally rotating molecules. An alternate approach to this problem may be developed when it is noted that, if high enough energies are considered, the auxiliary bending Schrödinger equation approaches that of one of the all-time-favourite examples of introductory Quantum Mechanics: a Particle In a (one-dimensional) Box (hereafter denoted "PIB") - with the difference that now the "mass" of the particle, $1/\mu_{\rho\rho}$, is position dependent.

$$(\partial^2/\partial\rho^2) \phi_K(\rho) = \left[\frac{2}{\hbar^2 \mu_{\rho\rho}} E \right] \phi_K(\rho). \quad (40)$$

In the case of HNN^+ , for example, the high energy limit can be interpreted as Hydrogen freely orbiting an NN unit. The present semirigid bender calculations for HNN^+ present a good opportunity for examining this idea. To do this a second approximation, after neglecting the effective potential energy in comparison with the energy eigenvalue, is to ig-

nore the rather larger variation of $\mu_{\rho\rho}$ with bending angle and instead to take some sort of average value $\langle\mu_{\rho\rho}\rangle$ as the constant value. By doing this the auxiliary bending Schrödinger equation becomes identical with that of a particle of fixed mass $1/\langle\mu_{\rho\rho}\rangle$ in a box of length $a = \pi$, and therefore has the eigenvalues,

$$\begin{aligned} E_n &= \frac{1}{2} \pi^2 \hbar^2 \langle\mu_{\rho\rho}\rangle (n^2/a^2) \\ &= \frac{1}{2} \hbar^2 \langle\mu_{\rho\rho}\rangle n^2 \\ &= 16.8576 \langle\mu_{\rho\rho} / \text{amu}^{-1} \text{ \AA}^{-2}\rangle n^2 \text{ cm}^{-1} \\ &= E_0 n^2. \end{aligned} \tag{41}$$

The question still remains of what would be a reasonable "average" $\langle\mu_{\rho\rho}\rangle$ to use in this context. The first point to note is that, as the energy is *linear* in $\mu_{\rho\rho}$, the average should be some sort of average of $\mu_{\rho\rho}$ and not, say, of $1/\mu_{\rho\rho}$. Also, as the Schrödinger equation, and therefore its eigenfunctions, are in terms of the bending angle ρ , whatever average is taken must be somehow averaged over ρ and *not* τ . Considering the problem classically one can say that, at a given energy eigenvalue E , the "velocity" of the "particle" at bending angle ρ , $v(\rho)$, is given in terms of the effective mass $m(\rho) = 1/\mu_{\rho\rho}(\rho)$ by,

$$v(\rho) = [2E/m(\rho)]^{1/2}. \tag{42}$$

This means that the "time" $t(\rho)$ that the particle "spends" at mass $m(\rho)$ is,

$$t(\rho) = 1/v(\rho) = [2E\mu_{\rho\rho}(\rho)]^{-1/2} \quad (43)$$

The "time" average of the inverse effective mass, $\langle \mu_{\rho\rho} \rangle$, over the range $\rho = 0$ to π , can thus be approximated in terms of the values at a discrete set of points ρ_n by,

$$\begin{aligned} \langle \mu_{\rho\rho} \rangle &= \sum_n t_n \mu_n / \sum_n t_n \\ &= \sum_n \mu_n^{-1/2} / \sum_n \mu_n^{-1/2}, \end{aligned} \quad (44)$$

where,

$$t_n = t(\rho_n),$$

$$\mu_n = \mu_{\rho\rho}(\rho_n),$$

and can be easily calculated once the bond length functions are specified. This calculation was done in the running of the semirigid bender program using the same grid of points as were used for the Numerov-Cooley numerical integration. For HNN⁺ $\mu_{\rho\rho}$ was found to vary from 0.27 to 1.24 amu⁻¹ Å⁻², while the "time" average was found to be $\langle \mu_{\rho\rho} \rangle = 0.70688$ amu⁻¹ Å⁻², giving $E_0 = 11.92$ cm⁻¹.

The question of importance is whether the *pattern* of energy levels predicted by the PIB approximation is in good agreement with the actual pattern. To answer this question the semirigid bender program was used to obtain the HNN⁺

bending energies and spacings in the regions $v_2 = 50$ and 100 (v_2 in *bent convention*, which, being simply the node count of the wavefunction, is related to the PIB quantum number by $v_2 = n-1$. For states with $\ell = 0$, $2v_2(\text{bent}) = v_2(\text{linear})$). These calculated energies and their first and second differences are presented in Table 36.

TABLE 36
HNN⁺/NNH⁺ Energy Level Pattern at Very High Energy
(cm⁻¹).

$v_2(\text{bent})$	$E(v_2)$	$\Delta E(v_2)$	$\Delta^2 E(v_2)$	E_0^a
48	33052.03			
49	34106.25	1065.43		
50	35182.89	1087.82	22.37	11.19
51	36281.90	1110.17		
52	37403.23			
98	112747.70			
99	114899.30	2162.55		
100	117072.80	2184.46	21.93	10.96
101	119268.21	2206.40		
102	121485.59			

^aDetermined by $E_0 = \frac{1}{2} \Delta^2 E(v_2)$.

The PIB energy level pattern is completely specified by the energies and their first and second differences which are determined by the single "spacing" constant E_0 and which are given by,

$$\begin{aligned}
 1. \quad E_n &= n^2 E_0, \\
 2. \quad \Delta E_n &= \frac{1}{2} (E_{n+1} - E_{n-1}) = 2n E_0, \\
 3. \quad \Delta^2 E_n &= \frac{1}{2} (\Delta E_{n+1} - \Delta E_{n-1}) = 2 E_0, \\
 4. \quad (\Delta^3 E_n &= 0).
 \end{aligned}
 \tag{45}$$

The formula for the second difference allows the calculation of E_0 from the semirigid bender (SRB) energies. The values thus obtained for $v_1 = 50$, and 100 are given in the last column of Table 36 and are in very good agreement with the value $E_0 = 11.92 \text{ cm}^{-1}$ which was obtained by the PIB approximation, purely from the assumed geometry of the molecule as it bends. It can also be seen that the second differences are remarkably constant, changing by less than 2% between $v_1 = 50$ and 100. Relations (3) and (4), above, are thus quite well satisfied.

Relations (1) and (2) are not expected to be in as good agreement until higher levels of v_1 . The level of agreement actually achieved, however, is still very good as is shown in Table 37 which compares the actual energies and differences obtained with the SRB model, with those calculated by the simple PIB approximation.

TABLE 37

HNN⁺/NNH⁺ Comparison of Vibrational Energies
Calculated with PIB and SRB Models (cm⁻¹).

Molecule	v_2	Model	E_0	$\Delta E(v_2)$	$E(v_2)$	$v_2(\text{calc})^a$
HNN ⁺ /NNH ⁺	50	SRB ^b	11.19	1088	35183	
		PIB ^c	11.92	1215	30994	53.3
	100	SRB	10.96	2184	117173	
		PIB	11.92	2407	121559	98.1

^aCalculated using $E(v_2)$ from the SRB calculation and then solving $E(v_2) \approx E_0(\text{PIB}) (v_2 + 1)^2$ for v_2 .

^bThe energy pattern calculated with the SemiRigid Bender.

^cThe energy pattern calculated with the Particle In a Box model.

Given an energy, and a value for E_0 , relation (1) can be solved for $v_2 = n-1$. The v_2 values thus obtained are given in the last column of Table 37 and show how good the PIB approximation is in the present case - at $v_2 = 100$ the PIB quantum number is off by only 2!

Table 38 gives the same comparisons at $v_2 = 100$ for the HCN/CNH, HCO⁺/COH⁺, and DCN/CNH molecules. The agreement

in these cases is as satisfactory as it was for $\text{HNN}^+/\text{NNH}^+$. In particular, the good agreement achieved for DCN/CND is especially significant as the mass of the orbiting Deuterium atom is about double that of the orbiting Hydrogen atom that is involved in the other molecules studied.

The conclusion from Table 36 is thus that at very high bending energy levels the vibrational energy level pattern can be well approximated by that of a particle of fixed mass in a box (Eq. 45). Further, from Table 37 and Table 38 it is seen that a reasonable estimate of the spacing constant E_0 can be obtained by calculating the "time" average of $\mu_{\rho\rho}$ as given by Eq. 44.

TABLE 38

HCN/CNH, DCN/CND, and HCO⁺/COH⁺ Comparison of PIB and SRB Vibrational Energies (cm⁻¹).

Molecule	v_2	Model	E_0	$\Delta E(v_2)$	$E(v_2)$	$v_2(\text{calc})^a$
HCN/CNH	100	SRB ^b	10.44	2083	113559	
		PIB ^c	11.35	2293	115777	99.0
HCO ⁺ /COH ⁺	100	SRB	10.36	2062	118502	
		PIB	11.14	2250	113616	102.1
DCN/CND	100	SRB	6.26	1244	71602	
		PIB	6.81	1376	69489	101.5
	200	SRB	6.45	2564	263855	
		PIB	6.81	2738	275210	195.8

^aCalculated using $E(v_2)$ from the SRB calculation and then solving $E(v_2) \approx E_0(\text{PIB}) (v_2 + 1)^2$ for v_2 .

^bThe energy pattern calculated with the SemiRigid Bender.

^cThe energy pattern calculated with the Particle In a Box model.

Appendix A

THE μ TENSOR.

In the semirigid bender model used in this work, the molecule-fixed z-axis was kept parallel to the CN moiety of the molecule. The elements of the inverse moment of inertia tensor $\mu_{\alpha\beta}$ are therefore different from those of HBJ [1970], Bunker and Stone [1972], and Bunker and Landsberg [1977]. The elements of $\mu_{\alpha\beta}$ are given below for *arbitrary choice of the angle ϵ* . Fig. 24 shows the labelling convention used in these expressions. Primes denote differentiation with respect to ρ , and the expressions actually used for the work reported in this thesis may be obtained by setting $\epsilon = 0$ and $\epsilon' = 0$. The first quantities given are the elements of the moment of inertia tensor I .

(46)

$$m = m_1 + m_2 + m_3$$

$$u_1 = m_1(m_2+m_3) r_1^2$$

$$u_2 = m_2(m_1+m_3) r_2^2$$

$$u_{12} = m_1 m_2 r_1 r_2$$

$$I_{xx} = [u_1 + u_2 + 2 u_{12} \cos \rho] / m$$

$$I_{yy} = [u_1 \cos^2(\rho-\epsilon) + u_2 \cos^2 \epsilon + 2 u_{12} \cos(\rho-\epsilon) \cos \epsilon] / m$$

$$I_{zz} = [u_1 \sin^2(\rho-\epsilon) + u_2 \sin^2 \epsilon - 2 u_{12} \sin(\rho-\epsilon) \sin \epsilon] / m$$

$$I_{yz} = \frac{1}{2} [u_1 \sin 2(\rho-\epsilon) - u_2 \sin 2\epsilon + 2 u_{12} \sin(\rho-2\epsilon)] / m$$

$$I_{x\rho} = -\epsilon' I_{xx} + [u_1 + u_{12} \cos \rho] / m - m_1 m_2 [r_1 r_2' - r_2 r_1'] (\sin \rho) / m$$

$$I_{\rho\rho} = -(\epsilon')^2 I_{xx} - 2 \epsilon' I_{x\rho} + [u_1 + 2 m_1 m_2 (r_1' r_2' \cos \rho - r_1 r_2' \sin \rho) + m_1 (m_2+m_3) (r_1')^2 + m_2 (m_1+m_3) (r_2')^2] / m$$

The effective inverse moment of inertia tensor for $Q_1 = Q_2 = 0$ is denoted μ^0 and is equal to the inverse of the moment of inertia tensor. As μ^0 is the quantity always used in this work, the superscript zero is neglected.

$$\begin{aligned}
 \mu_{xx} &= I_{\rho\rho} / (I_{xx}I_{\rho\rho} - I_{x\rho}^2) \\
 \mu_{yy} &= I_{zz} / (I_{yy}I_{zz} - I_{yz}^2) \\
 \mu_{zz} &= I_{yy} / (I_{yy}I_{zz} - I_{yz}^2) \\
 \mu_{yz} &= - I_{yz} / (I_{yy}I_{zz} - I_{yz}^2) \\
 \mu_{\rho\rho} &= I_{xx} / (I_{xx}I_{\rho\rho} - I_{x\rho}^2) \\
 \mu_{x\rho} &= - I_{x\rho} / (I_{xx}I_{\rho\rho} - I_{x\rho}^2)
 \end{aligned}
 \tag{47}$$

Appendix B.

NUMEROV-COOLEY NUMERICAL INTEGRATION.

The Numerov-Cooley technique of numerical integration (Cooley [1961]) may be used to solve the second-order non-linear homogeneous differential equation,

$$y''(x) = [f(x) - g(x) E] y(x), \quad (48)$$

where $y(x)$ is an eigenfunction and E is its eigenvalue. $y(x)$ may, in some instances, be an auxiliary function related to a principal function $Y(x)$ by,

$$y(x) = h(x) Y(x). \quad (49)$$

This is done, for example, in the semirigid bender equation to remove the first-order term which appears in the differential equation for the actual bending wavefunction.

In the present work a slight rearrangement of the basic integration formulae of Cooley [1961] was found to be somewhat simpler in form and use. This slightly modified Numerov-Cooley procedure is presented below.

The first step is to divide the interval $[a,b]$, over which the integration is to occur, into $m-1$ equal intervals by defining m equally spaced points,

$$\begin{aligned} x_n, n &= 1, 2, \dots, m, \\ x_1 &= a, \\ x_m &= b, \end{aligned} \quad (50)$$

which therefore have the spacing,

$$d = x_{n+1} - x_n = (a - b) / (m - 1). \quad (51)$$

The following quantities are then defined,

$$\begin{aligned} y_n &= y(x_n), \\ f_n &= f(x_n), \\ g_n &= g(x_n), \\ a_n &= [1 - d^2 (f_n - g_n E)/12]. \end{aligned} \quad (52)$$

The Numerov-Cooley integration formulae for forward (+) and backward (-) integration are then,

$$\begin{aligned} (+) y_n^+ &= [(12 - 10 a_{n-1}) y_{n-1} - a_{n-2} y_{n-2}] / a_n, \\ (-) y_n^- &= [10 a_{n+1} y_{n+1} - a_{n+2} y_{n+2}] / a_n. \end{aligned} \quad (53)$$

The procedure is to then,

1. Assume values for y_1 , y_2 , and y_{m-1} , y_m (for examples see Table 39), and a trial value for the energy eigenvalue E ,

2. Integrate from one end of the interval $[a,b]$ using the appropriate integration formula (+ or -) until the solution for $y(x)$ "turns over", that is, until it reaches its first local maximum. This point is labelled c and is called the "matching point".
3. The other integration formula (- or +) is then used to integrate from the other end of the interval $[a,b]$ just to the matching point c . The sets of points obtained in the forward and backward integrations are labelled y_+^* and y_-^* respectively.
4. Each of the two sets of points is in turn uniformly scaled so that at the matching point c they equal 1,

$$\begin{aligned} y_+^*(\text{new}) &= y_+^*(\text{old}) / (y_c^*), \\ y_-^*(\text{new}) &= y_-^*(\text{old}) / (y_c^-), \\ \text{then: } y_c^+ &= y_c^- = 1. \end{aligned} \tag{54}$$

5. The energy is corrected by using the formula,

$$\begin{aligned} \Delta E = & \left[-a_{c-1} y_{c-1} - a_{c+1} y_{c+1} \right. \\ & \left. + (12 - 10 a_c) y_c \right] a_c y_c \\ & \cdot [2 d^2 \sum_n^n g_n y_n^{-2}]^{-1}, \\ E(\text{new}) &= E(\text{old}) + \Delta E. \end{aligned} \tag{55}$$

6. Steps (2) to (5) are repeated until ΔE is smaller than the required precision of the eigenvalue.

7. The normalized principal wavefunction $Y(x)$ is calculated by,

$$Y(x_n) = [d \sum_i (y_i^2 / h_i^2)]^{-1/2} h_n y_n, \quad (56)$$

at which time the number of nodes of $Y(x)$ are counted. The node count is, by definition, the principal quantum number of this eigenfunction. For $h(x) = 1$ ($Y(x) = y(x)$), the normalization equation becomes the standard formula for the normalization of $y(x)$,

$$y(x_n) = [d \sum_i y_i^2]^{-1/2} y_n. \quad (57)$$

The simplification involved in the procedure that has been presented here is that there is no introduction of the "Y" variables - although the fourth-order correction (see Cooley [1961], who references Numerov [1933]) is still being used. This fourth order correction is now contained implicitly in the revised integration formulae which are no more complicated than those that do use the "Y" variables.

Two problems in this thesis were solved using the Numerov-Cooley technique, the semirigid bender (SRB) (Eq. 13) and the anharmonic oscillator (ANH) (Eq. 33). The specification of these two problems is given in Table 39.

Details of the use of the Numerov-Cooley technique for the semirigid bender model involving a double minimum potential function are given by Bunker and Howe [1980].

TABLE 39

Numerov-Cooley Numerical Integration.

Factor	Semirigid Bender ^a	Anh ^b
f	$f_1(\rho) + K^2 f_2(\rho) + \frac{2}{\hbar^2 \mu_{\rho\rho}} V_{\text{eff}}(\rho)$	$\frac{2}{\hbar^2 \mu} V(r)$
g	$\frac{2}{\hbar^2 \mu_{\rho\rho}}$	$\frac{2}{\hbar^2 \mu}$
h	$(\mu_{\rho\rho})^{-1/2}$	1
[a,b]	$[0, \pi]^c$	$[r_i, r_f]^d$
y_1, y_m	set by series solution	0
y_2, y_{m-1}	set by series solution	$10^{-20} e$

^aThis column gives the factors specifying the auxiliary Schrödinger equation for the Semirigid Bender model.

^bThis column gives the factors specifying the Schrödinger equation for the Anharmonic oscillator.

^cThe first and last thirty points of the numerical integration were actually obtained by using a series solution technique. The two outside points from the series solutions were used as the terminal values for the numerical integration.

^dThe interval $[r_i, r_f]$ for the numerical integration was chosen so that $V(r_i)$ and $V(r_f)$ were at least ten times larger than the largest eigenvalue considered.

^eIn principle any arbitrary values would suffice. By choosing such moderately small values the occurrence of numerical over - or under - flowing can be reduced.

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A separate list of references is located in Table 11 given near the end of Chapter II.

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