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# Variational calculations of rovibrational states: a precise high-energy potential surface for HCN

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We report the results of variational calculations of the rovibrational energy levels of HCN for  $J = 0, 1$  and  $2$ , where we reproduce all the *ca.* 100 observed vibrational states for all observed isotopic species, with energies up to  $18000\text{ cm}^{-1}$ , to about  $\pm 1\text{ cm}^{-1}$ , and the corresponding rotational constants to about  $\pm 0.001\text{ cm}^{-1}$ . We use a hamiltonian expressed in internal coordinates  $r_1$ ,  $r_2$  and  $\theta$ , using the exact expression for the kinetic energy operator  $T$  obtained by direct transformation from the cartesian representation. The potential energy  $V$  is expressed as a polynomial expansion in the Morse coordinates  $y_i$  for the bond stretches and the interbond angle  $\theta$ . The basis functions are built as products of appropriately scaled Morse functions in the bond-stretches and Legendre or associated Legendre polynomials of  $\cos \theta$  in the angle bend, and we evaluate matrix elements by Gauss quadrature. The hamiltonian matrix is factorized using the full rovibrational symmetry, and the basis is contracted to an optimized form; the dimensions of the final hamiltonian matrix vary from  $240 \times 240$  to  $1000 \times 1000$ . We believe that our calculation is converged to better than  $1\text{ cm}^{-1}$  at  $18000\text{ cm}^{-1}$ . Our potential surface is expressed in terms of 31 parameters, about half of which have been refined by least squares to optimize the fit to the experimental data. The advantages and disadvantages and the future potential of calculations of this type are discussed.

## 1. Introduction

The calculation of vibration–rotation energy levels and wavefunctions for a polyatomic molecule at high vibrational energy, which is closely related to our understanding of molecular dynamics, remains a major unsolved problem in molecular physics. In this context we assume that the potential energy surface is given; a polyatomic molecule means three or more atoms, and high vibrational energy means above  $10000\text{ cm}^{-1}$  (i.e.  $120\text{ kJ mol}^{-1}$ ), which is only about 25% of a typical chemical bond dissociation energy.

The traditional approach to this problem is to first solve the problem of small amplitude vibrations in the harmonic approximation (Wilson 1939; Wilson *et al.* 1955), and then to treat anharmonicity as a perturbation to this zeroth order model (Nielsen 1951; Mills 1971; Hoy *et al.* 1972; Papousek & Aliev 1982; Aliev & Watson 1985). Although this method provides a framework for the analysis of vibration–rotation spectra, it fails at high vibrational excitation for two reasons. First, the curvilinear nature of the natural coordinates of molecular vibration, and the deviation from harmonic behaviour in the potential (particularly for the approach to

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bond dissociation in stretching coordinates), become too large for a perturbation treatment at high energy. It becomes necessary to pursue the perturbation theory to high order, which leads to complex formulae and major problems of convergence in the resulting power series expansions. Secondly, for a polyatomic molecule the density of vibrational states grows rapidly at high energy, and the perturbations lead to increasingly frequent resonances for which the interactions are stronger than the separations between the zeroth-order states. The usual approach to this problem is to first treat the weak interactions by perturbation theory, using a contact transformation to obtain a hamiltonian matrix which is blocked into resonating polyads, and then to diagonalize these remaining blocks of the hamiltonian matrix numerically. This has developed into a standard procedure for treating Fermi and Coriolis resonance at low vibrational energy, although it requires specific programming for each molecule (see, for example, Champion *et al.* 1982; Halonen *et al.* 1984). With the inclusion of Darling–Dennison resonance to take account of the transition to local modes (Child & Lawton 1981; Child & Halonen 1984; Mills & Robiette 1985) the method has been extended to interpret observed vibrational states (but not rotational structure) up to  $15000\text{ cm}^{-1}$  (see, for example, Dübal & Quack 1984; Amrein *et al.* 1985; Baggott *et al.* 1986), but it is clear that the interaction constants obtained from such analyses are effective constants that are difficult to interpret.

However, even for a triatomic molecule such as HCN, discussed in this paper, the total density of vibrational states is of the order 1 per  $\text{cm}^{-1}$  at  $15000\text{ cm}^{-1}$ , and for molecules with four or five atoms this rises to the order of  $10^3$  per  $\text{cm}^{-1}$  (see Beyer & Swinehart (1973) and Stein Rabinovitch (1973) for a discussion of the calculation of densities of vibrational states); by contrast, the coupling terms increase in magnitude for the higher quantum numbers, and are often greater than  $1\text{ cm}^{-1}$ . Thus we approach the situation where resonances are the rule rather than the exception, and the basis of the perturbation treatment is lost; this is the reason for the ‘irregular’ or ‘chaotic’ patterns of states at high energy. However, some order and regularity remain amongst the disorder even at the highest energies, and these regular states play a key role in the spectroscopy and dynamics of highly excited molecules. We search for new methods of calculating wavefunctions and energies at high excitation that will meet these problems.

In this paper we describe our attempts to calculate rovibrational energy levels and wavefunctions variationally, by diagonalizing the matrix of the hamiltonian in a carefully chosen basis. We are applying these methods to 3-atomic and 4-atomic molecules such as HCN,  $\text{HC}\equiv\text{CH}$ , and  $\text{HO}-\text{OH}$ , and we are attempting to do exact calculations from a well-defined potential surface that reproduce spectroscopic observations within experimental uncertainty. We report here the results of our calculations on HCN, where we are at present reproducing all the *ca.* 100 observed vibrational states for all observed isotopic species, with energies up to  $18000\text{ cm}^{-1}$ , to about  $\pm 1\text{ cm}^{-1}$ , and the corresponding rotational constants to about  $\pm 0.001\text{ cm}^{-1}$ .

Other workers have also been applying these methods, although so far only for 3-atomic molecules and using somewhat different techniques (see, for example, Whitehead & Handy 1975; Carney *et al.* 1978; Sutcliffe 1982; Tennyson & Sutcliffe 1982; Burden & Quiney 1984; Bačić & Light 1987, 1989; Jensen 1983, 1988*a,b*, 1989). Tennyson *et al.* (this Symposium) are reporting variational calculations of a different type at this meeting. Our own program has been developing over the past few years, as we have reported in previous publications (Carter *et al.* 1983; Carter &

Handy 1982, 1986*a, b*; Senkowitsch *et al.* 1989). However, this is the first paper in which we have made a serious attempt to fit a wide range of spectroscopic data on a well studied molecule up to high energy (18000  $\text{cm}^{-1}$ ) with experimental precision.

## 2. Method of calculation

We express the rovibrational hamiltonian as the sum of kinetic energy  $T$  and potential energy  $V$  expressed in curvilinear internal coordinates  $r_1, r_2$  and  $\theta$  (being the C-H and C-N bond lengths and the H-C-N angle) and the total angular momentum operator  $\hat{J}$  and its molecule fixed components  $\hat{J}_x, \hat{J}_y$  and  $\hat{J}_z$ . We use basis functions constructed as products of Morse functions of  $r_1$  and  $r_2$  and Legendre polynomials of  $\cos\theta$ , multiplied by the rotational basis functions  $\psi_{J,k,M}$  where  $J, k$  and  $M$  are the usual angular momentum quantum numbers. The quantum number  $k$ , the signed component of  $J$  about the molecular axis, is constrained to be equal to the vibrational angular momentum quantum number  $l$ , and the space-fixed component  $M$  is set to zero. The potential energy is set up analytically as a polynomial expansion in the morse coordinates  $y_1$  and  $y_2$ , and the displacement  $\Delta\theta$  from linearity in the H-C-N angle. Matrix elements of the hamiltonian are calculated by Gauss quadrature. The basis is contracted through preliminary calculations using effective hamiltonians in  $r_1$  and  $r_2$  only, and in  $\theta$  only, which are subsets of the full hamiltonian, and the final matrix of the full hamiltonian is set up and diagonalized in this contracted basis using the full rovibrational symmetry of the problem.

### (i) Kinetic energy

We use the exact rovibrational kinetic energy operator  $T$  for a 3-atomic molecule, expressed in internal coordinates, derived from the quantum mechanical expression in external cartesian coordinates by using the coordinate transformation to internal coordinates and the chain rule of partial differentiation. The explicit expression for  $T$  in this form is quoted in Carter *et al.* (1983) and in Carter & Handy (1986). This method was originally proposed by Sutcliffe (1982), and implemented for a 3-atomic molecule by Carter & Handy (1982) and by Carter *et al.* (1983). It is an alternative to working through the classical kinetic energy expression, using normal coordinates, and using the Podolsky transformation, as described by Wilson *et al.* (1955) and by Watson (1968). This method is perhaps less elegant than the Podolsky approach, and it does not lead to any general expression for  $T$  applicable to all molecules; it requires a separate computer program for each molecular type, and the algebraic expressions are complex. However, these disadvantages are offset by the advantage that the algebra can be handled by an algebraic manipulation program as recently demonstrated by Handy (1987), who has verified the expressions for 3-atomic molecules and provided the corresponding results for all 4-atomic structures. The implementation of the method in a computer program is then relatively straightforward, and the use of curvilinear internal coordinates rather than normal coordinates is more closely related to the forms of the vibrational wavefunctions.

### (ii) Potential energy

We require an analytical expression for the potential energy which is sufficiently flexible to reproduce the true potential surface with high accuracy over a wide range of coordinate space. We have chosen to use a polynomial expansion in the Morse coordinates  $y_1$  and  $y_2$ , and the angular displacement from linearity  $\Delta\theta$ , where

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$$y_i = 1 - \exp(-a_i \Delta r_i), \quad i = 1 \text{ or } 2,$$

$$\Delta r_1 = r(\text{CH}) - r_e(\text{CH}), \quad \Delta r_2 = r(\text{CN}) - r_e(\text{CN}), \quad (1)$$

and 
$$\Delta \theta = \pi - \theta, \quad (2)$$

These are displacement coordinates (all three are zero in equilibrium), but the  $y_i$  are related by a nonlinear transformation to the usual bond-length displacement coordinates  $\Delta r_i$  in such a manner that a quadratic expression in the displacement coordinate  $y_i$ ,

$$V_i = D_e y_i^2 \quad (3)$$

is a Morse potential with bond dissociation energy  $D_e$  and Morse anharmonicity constant  $a_i$ . The relation between  $y_i$  and  $\Delta r_i$  is such that  $\Delta r_i = 0$  corresponds to  $y_i = 0$ , but  $\Delta r_i = +\infty$  corresponds to  $y_i = +1$ . Thus a polynomial expansion in  $y_i$  has the correct convergence properties at bond lengths approaching dissociation, and the cubic, quartic, and higher terms in the expansion have only to provide the small correction necessary to convert a Morse function into the true section of the potential energy function in each bond stretching coordinate.

These coordinates have been used previously by a number of authors (see, for example, Halonen & Child 1982, 1988; Halonen 1989). Their advantage in representing the potential over a conventional polynomial expansion is shown in table 1, where the coefficients that define our final potential surface for HCN are presented in three different forms as defined in the equations below:

$$V = \sum_{i,j,k} B(ijk) y_1^i y_2^j \Delta \theta^k, \quad (4)$$

$$= \sum_{i,j,k} (1/i!j!k!) F(ijk) (y_1/a_1)^i (y_2/a_2)^j \Delta \theta^k, \quad (5)$$

$$= \sum_{i,j,k} (1/i!j!k!) f(ijk) \Delta r_1^i \Delta r_2^j \Delta \theta^k. \quad (6)$$

The coefficients  $B(ijk)$  have dimensions of energy, and are given in the first column of table 1 in  $E_h$ , where  $1 E_h = 1 \text{ hartree} = 4.359748 \text{ aJ}$ . The coefficients  $F(ijk)$  have dimensions (energy)/(length) $^n$ , where  $n = i + j$ ; they are given in the second column of the table in  $\text{aJ } \text{\AA}^{-n}$ †. Equations (5) and (6) are written in the form of a Taylor series expansion in the coordinates, which is the origin of the factor  $(1/i!j!k!)$ . Thus

$$F(ijk) = i!j!k! a_1^i a_2^j B(ijk). \quad (7)$$

For example,

$$F(320) = 12a_1^3 a_2^2 B(320),$$

or  $[F(320)/(\text{aJ } \text{\AA}^{-5})] = (12)(1.886098)^3 (2.244737)^2 (4.359748)[B(320)/E_h]$ .

The coefficients  $f(ijk)$  have the same dimensions as the  $F(ijk)$ ; they are given in the third column of the table in the same units as the  $F$ s, i.e.  $\text{aJ } \text{\AA}^{-n}$ . For the quadratic force constants ( $i + j + k = 2$ ) the  $F(ijk)$  and the  $f(ijk)$  are identical (because  $y_i/a_i = \Delta r_i$  for small displacements), but for higher power terms the relations are obtained by using equation (1) to expand  $y_1$  and  $y_2$  in terms of  $\Delta r_1$  and  $\Delta r_2$  and substituting in equation (5). For example,

$$f(320) = 12a_1^3 a_2^2 \{B(320) - B(220) + \frac{1}{6}B(120) - \frac{1}{2}B(310) + \frac{1}{2}B(210) - \frac{1}{12}B(110)\}. \quad (8)$$

†  $1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-1} \text{ nm}$ .



## Potential surface for HCN

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Table 1. Parameters defining our final potential surface for HCN

(See text equations (4), (5) and (6). The  $B(ijk)$  values should be taken as definitive, with  $a_r = 1.886098 \text{ \AA}^{-1}$  and  $a_R = 2.244737 \text{ \AA}^{-1}$ . The indices  $i, j$  and  $k$  define the powers of coordinates associated with  $\Delta r(\text{CH})$ ,  $\Delta R(\text{CN})$ , and  $\Delta\theta$  respectively. Force constants marked \* were refined in the least squares calculation.)

$(ijk)$	$B(ijk)/E_h$	$F(ijk)/(\text{aJ } \text{\AA}^{-n})$	$f(ijk)/(\text{aJ } \text{\AA}^{-n})$
(200)	0.2013000	6.24401	$f_{rr}$ 6.2440
(110)	-0.0108352	-0.20000	$f_{rR}$ -0.2000
(020)	0.4248417	18.66593	$f_{RR}$ 18.6660
(300)	-0.0002253	-0.03954	$f_{rrr}$ -35.3700
(210)	-0.0048431	-0.33722	$f_{rRr}$ 0.0400
(120)	-0.0004700	-0.03895	$f_{rRR}$ 0.4100
(030)	-0.0008436	-0.24960	$f_{RRR}$ -125.9500
(400)*	0.0193775	25.65828	$f_{rrrr}$ 181.5913
(310)*	-0.0043949	-1.73149	$f_{rRrR}$ -0.5349
(220)*	0.0030858	0.96460	$f_{rRRR}$ 0.9483
(130)*	0.0007613	0.42484	$f_{rRRR}$ -0.3206
(040)*	0.0037820	10.04746	$f_{RRRR}$ 671.7925
(500)*	0.0042663	53.27401	— = 1062.5595
(410)*	-0.0052727	-15.67214	— = 3.1329
(320)*	-0.0004324	-0.76481	— = 5.1607
(230)*	-0.0000718	-0.15114	— = 7.7414
(140)*	-0.0026729	-13.39312	— = 18.2267
(050)*	0.0002364	7.04884	— = 3416.8563
(600)*	0.0050242	709.98058	— = 7609.1184
(510)*	-0.0051484	-144.31181	— = 28.6991
(420)	0.00*	0.00*	— = 39.9690
(330)*	-0.0000799	-0.95170	— = 41.5584
(240)	0.00*	0.00*	— = 74.2507
(150)*	0.0002227	12.52434	— = 368.2129
(060)*	-0.0001325	-53.21121	— = 17946.0818
(002)	0.0297734	0.25961	$f_{\theta\theta}$ 0.2596
(102)	-0.0115531	-0.19000	$f_{r\theta\theta}$ = 0.1900
(012)	-0.0332090	= 0.65000	$f_{R\theta\theta}$ = 0.6500
(202)*	-0.0040501	= 0.25126	$f_{rr\theta\theta}$ 0.1071
(112)*	0.0065146	0.24050	$f_{rR\theta\theta}$ 0.2405
(022)*	-0.0080516	= 0.70751	$f_{RR\theta\theta}$ 0.7516
(004)*	0.0003639	0.03808	$f_{\theta\theta\theta\theta}$ 0.03808
(006)*	-0.0001552	-0.48718	— = -0.48718

\* These two constants were kept constrained to zero in the refinement.

The  $f(ijk)$  are the conventional anharmonic force constants, as used, for example, by Strey & Mills (1973) in their anharmonic force constant calculation on HCN. The  $F$ 's are comparable with the  $f$ 's, but they show the advantage of representing the potential in Morse coordinates  $y_i$  rather than bond length displacements  $\Delta r_i$ . Thus all the higher power  $F$ 's are much smaller (of the order 5% or less) than the corresponding  $f$ 's. The polynomial expansion in the  $y$ 's converges more rapidly than in the  $\Delta r$ 's, and gives a true representation of the potential surface over a wider range with fewer terms. There are altogether 33 parameters in our specification of the potential energy surface, namely  $a_1$ ,  $a_2$ , and 31  $B$ 's (or  $F$ 's). The way in which these were chosen for our final potential is described in the following section. In the subroutine in our program the energy was calculated from the  $B$ 's using equation (4).

(iii) *Basis functions*

As in our earlier work, we have chosen the vibrational basis functions to be products of Morse oscillator eigenfunctions in the two stretching coordinates and Legendre polynomials (for  $k = 0$ ) or associated Legendre polynomials (for  $|k| \geq 1$ ) in the angle bend. These are multiplied by the usual symmetric top rotational functions of the Euler angles to give a complete set of rovibrational basis functions. A complete basis function might thus be written symbolically in the form (note that we are numbering the stretching coordinates 1 and 2, and the bending coordinate 3, contrary to spectroscopic convention)

$$\Phi(n_1, n_2, n_3, J, M, k) = \phi_{n_1}(r_1) \phi_{n_2}(r_2) \phi_{n_3}(\theta) \psi_{JMK}(\alpha, \beta, \gamma). \quad (9)$$

However, for the bond stretching coordinates of HCN we chose to use Morse functions of  $Q_1$  and  $Q_2$  rather than of  $\Delta r_1$  and  $\Delta r_2$ , where the  $Q_i$  are the mass adjusted normal coordinates obtained from a preliminary harmonic force field calculation for each isotopic species considered. When combined with the contraction procedure described below this resulted in stretching basis functions closer to the true vibrational eigenfunctions over the range we have considered. Our normalized Morse basis functions are thus given by the equations

$$\phi_n(Q_i) = N_n e^{-\frac{1}{2}\xi_i} \xi_i^s L_n^{2s}(\xi_i), \quad (10a)$$

$$N_n = [\alpha n! (2s - n) / \Gamma(k - v)], \quad (10b)$$

$$s = [(2m_i D_{ei})^{1/2} / \hbar \alpha_i] - (n + \frac{1}{2}), \quad (11)$$

$$\xi_i = 2[(2m_i D_{ei})^{1/2} / \hbar \alpha_i] \exp(-\alpha_i Q_i), \quad (12)$$

$$Q_i = \sum_j (L^{-1})_{ij} \Delta r_j, \quad i, j = 1, 2. \quad (13)$$

The  $L_n^{2s}(\xi_i)$  in equation (10a) are associated Laguerre polynomials, and  $N_n$  are normalization constants. The effective masses  $m_i$  associated with the coordinates  $Q_i$  are actually 1 (because the  $Q_i$  are mass adjusted). The parameters  $\alpha_i$  and  $D_{ei}$  that characterize the Morse function in  $Q_i$  are listed in table 2; they were chosen to match the approximate Morse characteristics of the dominant bond stretch in each normal coordinate. The  $L$  matrix elements used to define the transformation in equation (13) for each isotopic species, and the assumed molecular geometry, are also listed in table 2.

Table 2. *Parameters used to define the structure and the primitive basis functions for various isotopic species of HCN*

( $r_e(\text{CH}) = r_1 = 1.0655 \text{ \AA}$ ,  $r_e(\text{CN}) = r_2 = 1.1532 \text{ \AA}$ .  $L$  matrix elements used to define the stretching normal coordinates,  $\Delta r_i = L_{ij} Q_j$ , where  $r_1$  and  $r_2$  denote displacements in  $r(\text{CH})$  and  $r(\text{CN})$ ; and  $\alpha_i$  parameters used to define the Morse basis functions, equations (11, 12).)

	1-12-14	1-13-14	1-12-15	2-12-14
$L_{11}/u^{1/2}$	1.0246	1.0236	1.0246	0.6788
$L_{12}/u^{1/2}$	0.1604	0.1460	0.1604	0.3451
$L_{21}/u^{1/2}$	-0.1389	-0.1270	-0.1389	-0.2688
$L_{22}/u^{1/2}$	0.3680	0.3636	0.3680	0.2872
$\alpha_1/(u^{-1/2} \text{ \AA}^{-1})$	1.8289	1.8943	1.8289	1.4527
$\alpha_2/(u^{-1/2} \text{ \AA}^{-1})$	0.8653	0.8588	0.8653	0.8013

The angular basis functions  $\phi_{n_3}^{(\theta)}$  are the functions  $\Theta_{n_3}^l(\theta)$  related to the associated Legendre functions  $P_{n_3}^l(\cos \theta)$  by the equation

$$\Theta_{n_3}^l(\theta) = (-1)^l \left[ \frac{(2n_3+1)(n_3-l)!}{2(n_3+l)!} \right] P_{n_3}^l(\cos \theta), \quad (14)$$

see equation (1.52) in Zare (1988). For negative values of  $l$  the factor  $(-1)^l$  on the right-hand side of (14) should be omitted (Zare 1988). The quantum number  $n_3$  is related to the customary linear angle bend quantum numbers  $(v_3, l)$  by the equation

$$v_3 = 2n_3 - |l|, \quad (15)$$

where  $l$  is the vibrational angular momentum about the axis,  $v_3 \geq |l|$ , and  $v_3$  is of the same parity as  $l$ . The functions  $\Theta_{n_3}^l(\theta)$  are linked to the rotational basis functions  $\psi(\alpha, \beta, \gamma) = D_{0k}^J(\beta, \gamma)$  such that  $l = k$ . (Note that  $k$  is not a good quantum number for the final eigenfunctions, although it is a good quantum number for our basis functions.) Only the rotational functions  $D_{Mk}^J(\alpha, \beta, \gamma) = D_{0k}^J(\beta, \gamma)$  with  $M = 0$  are used. (It is important to ensure that consistent phase conventions are used for the bending vibrational basis functions  $\Theta_{n_3}^k(\theta)$  and the rotational basis functions  $D_{0k}^J(\beta, \gamma)$ . This particularly applies when we come to calculate transition moments and intensities.)

This choice for the angular basis functions has the desired symmetry properties at  $\theta = 0$  and  $\pi$ , but it has the disadvantage that they are not optimized to represent the bending eigenfunctions for any particular form of the bending potential, in contrast to our choice for the stretching vibrational basis functions. We therefore have to use a large number of angle bending functions in our initial formulation of the basis. This is overcome by contracting the basis as described in the following section.

At this stage a complete rovibrational basis function may be written in the form

$$\Phi(n_1, n_2, v_3, l_3; J, k) = \phi_{n_1}(Q_1) \phi_{n_2}(Q_2) \Theta_{n_3}^k(\theta) D_{0k}^J(\beta, \gamma), \quad (16)$$

where  $l_3$  has been set equal to  $k$ . For the final basis functions we form Wang combinations of the functions (14) with positive and negative values of  $k$ , in order to make use of the full  $\Sigma^+$  or  $\Sigma^-$  symmetry of the wavefunctions (where  $\Sigma^+$  is denoted e and  $\Sigma^-$  is denoted f for  $J$  even, and vice-versa for  $J$  odd (see Brown *et al.* 1975)).

#### (iv) Calculation of matrix elements: contraction of the basis

All integrals of the kinetic energy over the vibrational coordinates were carried out numerically by one-dimensional Gauss quadrature (Golub & Welsch 1969). The integrals over the rotational matrix elements were calculated analytically using standard angular momentum formulae. For the Morse stretching basis functions the Gauss integration points were expressed in terms of the variable  $\xi_i$ , and for the angle bending functions in terms of the variable  $\cos \theta$ .

For the integrals over the potential energy we used a modified integration procedure based on a combination of the method of Harris *et al.* (1965), the HEG method, and a scheme proposed by Schwenke & Truhlar (1984). In the HEG method the eigenvalues of the matrix of each coordinate in the chosen basis functions are used to determine the quadrature points, and in the Schwenke & Truhlar scheme the weights associated with these points are obtained by solving a set of linear equations constructed from the basis functions and the particular quadrature points used. This procedure produces quadrature points and weights superior to the original Gauss



points and weights, for basis functions chosen to be close to the true eigenfunctions, since they are optimized to the potential via the optimized basis functions. Further details of our Gauss integration procedure are given in §6 of Carter & Handy (1986).

Our angle bending basis functions, being chosen as Legendre or associated Legendre polynomials, are not initially optimized to any bending potential. We therefore set up and diagonalize a preliminary one-dimensional hamiltonian over 31 bending basis functions only, for each value of  $k$  (omitting from the hamiltonian at this stage those terms that couple different values of  $k$ ), and use the 13 lowest energy eigenvectors of this matrix as a contracted set of optimized bending basis functions for each  $k$ . The HEG Schwenke–Truhlar integration procedure is used only with these optimized bending functions. A similar contraction of the basis is made for the two stretching coordinates: we use 16 Morse functions in each stretching coordinate to give an initial basis of  $16^2 = 256$  stretching functions, and we take the 54 lowest energy eigenfunctions of the stretching hamiltonian in this basis as a contracted set of stretching basis functions.

The 13 contracted bending functions are then combined with the 54 contracted stretching functions to give a basis of dimension  $13 \times 54 = 702$  stretch–bend functions for each value of  $k$ . The eigenfunctions of the hamiltonian in this basis are used to set up the final matrix of the full hamiltonian, for each symmetry (e or f) and for each value of  $J$ , in which different values of  $k$  are coupled together. The dimensions of the basis at each stage of contraction are summarized in table 3.

Table 3. *The dimensions of the basis set at successive stages of contraction*

(See text. A right arrow ( $\rightarrow$ ) is used to denote contraction by taking the lowest energy eigenfunctions of the previous basis as a new basis set.)

$Q_1$	$Q_2$	$Q_1 Q_2$ basis	$\theta$ basis	$Q_1 Q_2 \theta$ basis
$16 \times 16$	=	$256 \rightarrow 54$ ;	$31 \rightarrow 13$ ;	$54 \times 13 = 702$
		$Q_1 Q_2 \theta$ basis		symmetrized $Q_1 Q_2 \theta$ basis
$J = 0, k = 0$ :		$54 \times 13 = 702$	$\rightarrow$	e: 702
$J = 1, k = 0$ :		$54 \times 13 = 702$	$\rightarrow$	e: 500
$k = 1$ :		$54 \times 13 = 702$	$\rightarrow$	f: 241
$J = 2, k = 0$ :		$54 \times 13 = 702$	$\rightarrow$	e: 1000
$k = 1$ :		$54 \times 13 = 702$	$\rightarrow$	f: 645
$k = 2$ :		$54 \times 13 = 702$	$\rightarrow$	

These procedures of successive contraction of the basis enable us to achieve a degree of convergence that would otherwise be impossible with hamiltonian matrices of dimensions less than  $1000 \times 1000$ .

(v) *Convergence of results: least squares refinement procedure*

The whole of the calculation described thus far proceeds from an assumed form of the potential energy, specified by the parameters described in §2(ii) above, to vibration–rotation eigenvalues and eigenfunctions (the latter being specified through the eigenvectors as linear combinations of our basis functions). By the variation theorem this yields a set of eigenvalues that must each be greater than the corresponding true eigenvalue when taken in one-to-one correspondence in order of energy (MacDonald 1933). (There is a reservation to be made about the application of this theorem to our problem: we have effectively truncated our bending

Potential surface for HCN

Table 4. Observed and calculated vibrational term values and rotational constants for four isotopic species of HCN, all in  $\text{cm}^{-1}$ . (The final two columns give the differences  $\Delta G(v) = G_{\text{obs}} - G_{\text{calc}}$  and  $\Delta B(v) = B_{\text{obs}} - B_{\text{calc}}$ . The observed data are taken from Smith *et al.* (1989) and other references therein. Note that the vibrational quantum numbers in the first column are in the form  $(v_1, v_2^{\pm}, v_3)$ .)

assignment	$G(v)$	sym	$B(\text{eff})$	$\Delta(B)$	calculated data/ $\text{cm}^{-1}$						obs-calc	
					$J=0$	$J=1$		$J=2$		$\Delta G(v)$	$\Delta B(v)$	
$\Sigma$ 0 <sup>0</sup> 0	0.00	e	1.478222	1.478222	1e	0.000	1e	2.958	1e	8.874	0.00	-0.001
$\Pi$ 0 <sup>1</sup> 0	713.46	e	1.478028	-0.000194	2e	715.045	2e	715.045	2e	720.943	-0.11	0.003
$\Sigma$ 0 <sup>2</sup> 0	1411.43	e	1.485516	0.007294	1f	1411.686	1f	1411.686	1f	1420.616	-0.26	-0.002
$\Delta$ 0 <sup>2</sup> 0	1432.47	e	1.485007	0.006785	2e	1411.686	3e	1414.663	3e	1420.616	-0.26	-0.002
$\Sigma$ 1 <sup>0</sup> 0	2096.85	e	1.468150	-0.010072	3e	2096.728	4e	2099.666	2f	1435.451	-0.01	0.000
$\Pi$ 0 <sup>3</sup> 0	2114.94	e	1.478019	-0.000203	5e	2116.615	5e	2116.615	6e	2122.524	-0.21	0.001
$\Phi$ 0 <sup>3</sup> 0	2802.96	ef	1.501146	0.022924	2f	2116.656	2f	2116.656	3f	2122.651	0.08	0.003
$\Sigma$ 0 <sup>4</sup> 0	2807.06	e	1.487897	0.009675	4e	2803.160	6e	2806.155	7e	2812.143	-0.20	-0.003
$\Pi$ 1 <sup>1</sup> 0	2807.06	e	1.493843	0.015621	7e	2808.903	7e	2808.903	8e	2814.770	-0.38	0.001
$\Delta$ 0 <sup>4</sup> 0	2824.16	f	1.467831	-0.010391	3f	2808.921	3f	2808.921	4f	2814.824	0.08	-0.001
$\Gamma$ 0 <sup>4</sup> 0	3311.48	ef	1.475314	-0.002908	5e	3310.485	8e	3313.421	10e	3319.291	0.99	0.000
$\Sigma$ 0 <sup>5</sup> 0	3496.69	e	1.492964	0.014742	6e	3502.657	9e	3498.108	11e	3504.028	0.04	-0.002
$\Pi$ 0 <sup>5</sup> 0	3496.69	e	1.492964	0.014742	6e	3502.657	10e	3505.613	12e	3511.522	-0.53	0.006
$\Sigma$ 1 <sup>2</sup> 0	3502.13	e	1.474668	-0.003554	11e	4006.200	11e	4006.200	13e	4204.465	0.03	-0.002
$\Delta$ 1 <sup>2</sup> 0	3522.78	ef	1.467749	-0.010473	14e	4006.217	14e	4006.217	14e	4012.063	0.90	0.002
$\Pi$ 0 <sup>1</sup> 1	4005.64	e	1.475311	-0.002911	7e	4172.419	5f	4175.336	8f	4181.169	0.68	0.000
$\Sigma$ 2 <sup>0</sup> 0	4173.10	e	1.458032	-0.020190	8e	4174.647	12e	4177.661	15e	4183.683	-0.31	0.000
$\Sigma$ 0 <sup>6</sup> 0	4202.71	e	1.467890	-0.010332	13e	4174.647	13e	4177.661	16e	4183.683	-0.31	-0.002
$\Pi$ 1 <sup>3</sup> 0	4244.14	f	1.490399	0.012177	6f	4204.513	14e	4204.476	18e	4210.353	0.55	0.002
$\Phi$ 1 <sup>3</sup> 0	4684.32	ef	1.477444	-0.000778	9e	4683.764	15e	4686.716	19e	4692.618	0.85	0.000
$\Sigma$ 0 <sup>2</sup> 1	4684.32	e	1.475845	-0.002377								

Table 4. (*cont.*)

assignment	HCN 1-12-14, observed data/cm <sup>-1</sup>				calculated data/cm <sup>-1</sup>				obs-calc	
	$G(v)$	sym	$B(\text{eff})$	$\Delta(B)$	$J=0$	$J=1$	$J=2$	$\Delta G(v)$	$\Delta B(v)$	
$\Delta$ 0 <sup>2</sup> 1	4705.12	ef	1.475001	-0.003221			20e 11f	4707.167 4707.167	0.90	
$\Pi$ 0 <sup>7</sup> 0		e				16e	4859.696	4865.634		
$\Pi$ 2 <sup>1</sup> 0	4879.73	e	1.457578	-0.020644		7f	4859.776	4865.874		
$\Sigma$ 1 <sup>4</sup> 0		f	1.465006	-0.013216		17e	4881.490	4887.317	-0.30	0.001
$\Pi$ 0 <sup>3</sup> 1					10e	18e	4890.850	4896.797	0.14	0.000
$\Sigma$ 1 <sup>0</sup> 1	5393.70	e	1.457936	-0.020286		19e	5369.518	5375.396	-2.66	
$\Sigma$ 0 <sup>8</sup> 0					11e	9f	5369.551	5375.499	0.75	0.000
$\Sigma$ 2 <sup>2</sup> 0	5571.89	e			12e	20e	5395.866	5401.697		
$\Pi$ 1 <sup>5</sup> 0					13e	21e	5529.302	5535.360	-0.28	
$\Sigma$ 0 <sup>4</sup> 1	6084.80	e	1.457748	-0.020474		22e	5575.103	5580.969		
$\Pi$ 1 <sup>1</sup> 1	6228.59	e	1.447804	-0.030418		23e	5579.459	5585.347		
$\Sigma$ 3 <sup>0</sup> 0		f			14e	10f	5579.518	5585.522	-0.16	
$\Pi$ 2 <sup>3</sup> 0	6519.61	e	1.457084	-0.021138		24e	6040.129	6046.063	0.31	0.001
$\Sigma$ 0 <sup>0</sup> 2	6761.33	e				25e	6085.949	6091.776	1.59	0.000
$\Sigma$ 1 <sup>2</sup> 1	7194.23	e	1.457181	-0.021041		11f	6085.966	6091.826		
$\Pi$ 0 <sup>1</sup> 2	7455.42	e	1.448051	-0.030171		27e	6229.894	6235.686		
$\Sigma$ 2 <sup>0</sup> 1					15e	29e	6270.682	6276.516		
$\Pi$ 2 <sup>1</sup> 1	8585.57	e	1.447430	-0.030792		13f	6270.717	6276.531	0.80	0.001
$\Sigma$ 4 <sup>0</sup> 0	9257.56	e	1.447380	-0.030842		30e	6521.721	6527.547	0.65	0.001
$\Sigma$ 1 <sup>0</sup> 2					17e	30e	6521.721	6527.547		
$\Pi$ 1 <sup>1</sup> 2		f	1.455182	-0.023040		32e	6763.614	6769.478		
					18e	25e	6085.949	6091.776	0.31	0.001
					22e	11f	6085.966	6091.826	1.59	0.000
					28e	27e	6229.894	6235.686		
					30e	29e	6270.682	6276.516		
					17e	13f	6270.717	6276.531	0.80	0.001
					18e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001
					17f	11f	6085.966	6091.826	1.59	0.000
					40e	27e	6229.894	6235.686		
					22e	29e	6270.682	6276.516		
					28e	13f	6270.717	6276.531	0.80	0.001
					30e	30e	6521.721	6527.547	0.65	0.001
						32e	6763.614	6769.478		
					37e	25e	6085.949	6091.776	0.31	0.001

Potential surface for HCN

Table 4. (cont.)

assignment	HCN 1-12-14, observed data/cm <sup>-1</sup>				calculated data/cm <sup>-1</sup>				obs-calc	
	<i>G(v)</i>	sym	<i>B</i> (eff)	$\Delta$ ( <i>B</i> )	<i>J</i> = 0	<i>J</i> = 1	<i>J</i> = 2	$\Delta G(v)$	$\Delta B(v)$	
$\Sigma$ 3 <sup>0</sup> 1	9496.43	e	1.438028	-0.040194	38e 9495.302	70e 9498.178	97e 9503.928	1.13	0.000	
$\Sigma$ 0 <sup>0</sup> 3	9627.08	e	1.446034	-0.032188	39e 9626.962	72e 9629.852	99e 9635.633	0.12	0.001	
$\Sigma$ 1 <sup>2</sup> 2	9914.39	e	1.455630	-0.022592	42e 9915.109	77e 9918.021	106e 9923.844	-0.72	0.000	
$\Sigma$ 5 <sup>0</sup> 0	10281.84	e	1.446345	-0.031877	46e 10272.616	84e 10275.470	117e 10281.179			
$\Pi$ 0 <sup>1</sup> 3		e	1.446345	-0.031877		85e 10283.838	118e 10289.620	-0.55	0.001	
		f	1.454100	-0.024122		39f 10283.852	72f 10289.664		0.001	
$\Sigma$ 2 <sup>0</sup> 2	10631.44	e	1.437729	-0.040493	49e 10631.341	92e 10634.215	127e 10639.964	0.10	0.000	
$\Sigma$ 4 <sup>0</sup> 1		e			59e 11514.756	111e 11517.612	155e 11523.322			
$\Sigma$ 1 <sup>0</sup> 3	11674.45	e	1.436622	-0.041600	63e 11674.682	117e 11677.555	163e 11683.299	-0.23	0.001	
$\Sigma$ 6 <sup>0</sup> 0		e			70e 12256.210	131e 12266.428	183e 12265.286			
$\Sigma$ 0 <sup>0</sup> 4	12635.89	e	1.434456	-0.043766	75e 12635.918	141e 12638.786	198e 12644.516	-0.03	0.002	
$\Sigma$ 3 <sup>0</sup> 2	12657.88	e	1.428169	-0.050053	76e 12658.228	142e 12661.084	199e 12666.794	-0.35	0.001	
$\Pi$ 0 <sup>1</sup> 4	13270.79	e	1.435274	-0.042948		159e 13273.676	224e 13279.412	-1.46	0.001	
		f	1.443058	-0.035164		75f 13273.687	140f 13279.453		0.002	
$\Sigma$ 5 <sup>0</sup> 1		e			89e 13512.806	167e 13515.642	236e 13521.311			
$\Sigma$ 2 <sup>0</sup> 3	13702.25	e	1.427114	-0.051108	93e 13702.896	176e 13705.752	248e 13711.456	-0.65	0.001	
$\Sigma$ 4 <sup>0</sup> 2	14653.66	e	1.421947	-0.056275	108e 14652.719	206e 14655.571	292e 14661.251	0.94	0.002	
$\Sigma$ 1 <sup>0</sup> 4	14670.45	e	1.421680	-0.056542	109e 14671.696	207e 14674.546	293e 14680.222	-1.25	0.003	
$\Sigma$ 0 <sup>0</sup> 5	15551.94	e	1.423004	-0.055218	129e 15552.071	243e 15554.933	346e 15560.603	-0.13	0.006	
$\Sigma$ 3 <sup>0</sup> 3	15710.53	e	1.417569	-0.060653	132e 15711.721	251e 15714.569	356e 15720.224	-1.19	0.004	
$\Pi$ 6 <sup>1</sup> 1	16165.55	e	1.420214	-0.058008		267e 16164.117	380e 16169.731	2.85	0.017	
		f	1.427674	-0.050548		128f 16164.121	241f 16169.782		0.012	
$\Pi$ 0 <sup>1</sup> 5	16165.55	e	1.420214	-0.058008		268e 16169.560	381e 16175.233	-2.59	0.002	
		f	1.427674	-0.050548		129f 16169.546	242f 16175.267		-0.003	
$\Sigma$ 5 <sup>0</sup> 2	16640.31	e	1.409760	-0.068462	150e 16639.015	287e 16641.848	410e 16647.480	1.30	0.002	
$\Sigma$ 2 <sup>0</sup> 4	16674.21	e	1.414731	-0.063491	152e 16675.853	290e 16678.700	413e 16684.344	-1.64	0.004	
$\Sigma$ 1 <sup>0</sup> 5	17550.39	e	1.414119	-0.064103	175e 17549.587	333e 17552.612	478e 17558.107	0.81	0.040	
$\Sigma$ 0 <sup>0</sup> 6	18377.01	e	1.411041	-0.067181	198e 18376.543	378e 18379.586	542e 18385.029	0.46	0.050	
$\Sigma$ 0 <sup>0</sup> 0	0.00	e	1.439995	1.439995	1e 0.000	1e 2.881	1e 8.643	0.00	0.000	
$\Pi$ 0 <sup>1</sup> 0		e				2e 708.960	2e 714.706			
		f				1f 708.979	1f 714.768			
$\Sigma$ 0 <sup>2</sup> 0		e			2e 1400.039	3e 1402.937	3e 1408.730			

Table 4. (cont.)

assignment	HCN 1-12-14, observed data/cm <sup>-1</sup>				calculated data/cm <sup>-1</sup>				obs-calc	
	<i>G(v)</i>	sym	<i>B</i> (eff)	$\Delta$ ( <i>B</i> )	<i>J</i> = 0	<i>J</i> = 1	<i>J</i> = 2	$\Delta G(v)$	$\Delta B(v)$	
$\Delta$ 0 2 <sup>0</sup> 0		e					4e 1423.337			
$\Sigma$ 1 0 <sup>0</sup> 0		f			3e 2062.933	4e 2065.794	2f 1423.338			
$\Pi$ 0 3 <sup>1</sup> 0		e				5e 2099.367	5e 2071.515			
		e				2f 2099.405	6e 2105.123			
$\Pi$ 1 1 <sup>1</sup> 0	2766.74	f	1.429701	-0.010294		6e 2768.579	3f 2105.238			
		e	1.436897	-0.003098		3f 2768.595	7e 2774.295		0.001	
$\Sigma$ 0 0 <sup>1</sup> 1	3293.51	f	1.430365	-0.009630	5e 3292.551	8e 3295.411	4f 2774.344		0.000	
$\Pi$ 0 1 <sup>1</sup> 1	3983.65	e				11e 3982.742	10e 3301.132	0.96	0.000	
		e	1.436905	-0.003090	9e 4655.281	5f 3982.758	14e 3988.455	-0.52		
$\Sigma$ 0 2 <sup>0</sup> 1	4655.86	f				15e 4658.155	8f 3988.506	0.58	0.000	
$\Sigma$ 0 2 <sup>1</sup> 1	4680.78	e					19e 4663.904	5.43		
		e	1.420805	-0.019190	11e 5343.011		20e 4678.226			
$\Sigma$ 1 0 <sup>1</sup> 1	5343.66	f					11f 4678.226	0.65	0.000	
$\Pi$ 1 1 <sup>1</sup> 1	6030.21	e				20e 5345.853	26e 5351.535	-1.19		
		e	1.348815	-0.091180	17e 6482.505	11f 6029.994	34e 6035.656			
$\Sigma$ 0 0 <sup>2</sup> 2	6483.28	f				30e 6485.345	20f 6035.705	0.77	-0.071	
$\Pi$ 0 1 <sup>1</sup> 2	7154.49	e				37e 7153.933	40e 6491.025	-0.86		
		e	1.411076	-0.028919	30e 8519.024	17f 7153.948	50e 7159.610			
$\Sigma$ 1 0 <sup>2</sup> 2	8519.24	f					30f 7159.656	0.21	0.000	
$\Sigma$ 0 0 <sup>3</sup> 3	9571.69	e	1.410233	-0.029762	41e 9571.544	55e 8521.846	75e 8527.489	0.14	0.001	
$\Sigma$ 1 0 <sup>3</sup> 3	11591.42	e	1.401195	-0.038800	63e 11591.860	75e 9574.363	104e 9580.001	-0.44	0.001	
$\Sigma$ 0 0 <sup>5</sup> 5	15455.20	e	1.388841	-0.051154	131e 15455.018	118e 11594.662	165e 11600.264	0.18	0.006	
$\Sigma$ 3 0 <sup>3</sup> 3	15572.80	e	1.382539	-0.057456	132e 15574.550	247e 15457.812	351e 15463.345	-1.75	0.004	
$\Pi$ 0 1 <sup>1</sup> 5	16067.52	e	1.386339	-0.053656		251e 15577.327	356e 15582.842	-0.64	0.003	
		f	1.393416	-0.046579		272e 16069.547	386e 16075.082		-0.002	
$\Sigma$ 2 0 <sup>4</sup> 4	16544.28	e	1.381607	-0.058388	151e 16540.302	130f 16069.533	244f 16075.116	-1.53	0.004	
$\Sigma$ 1 6 <sup>5</sup> 5	17431.94	e	1.380128	-0.059867	176e 17431.396	290e 16549.083	413e 16554.593	0.54	0.038	
$\Sigma$ 0 0 <sup>6</sup> 6	18257.21	e	1.377695	-0.062300	198e 18256.131	336e 17434.346	482e 17439.714	1.08	0.049	
$\Sigma$ 0 0 <sup>0</sup> 0	0.00	e	1.435248	1.435248	1e 0.000	379e 18259.101	543e 18264.415	0.00	-0.001	
$\Pi$ 0 1 <sup>1</sup> 0		e				1e 2.872	1e 8.616			
		e				2e 714.004	2e 719.730			
		e				1f 714.024	1f 719.796			



Potential surface for HCN

Table 4. (cont.)

HCN 1-12-14, observed data/cm <sup>-1</sup>		calculated data/cm <sup>-1</sup>				obs-calc			
assignment	G(v)	sym	B(eff)	Δ(B)	J = 0	J = 1	J = 2	ΔG(v)	ΔB(v)
Σ 0 2 <sup>o</sup> 0					2e 1409.57	3e 1412.469	3e 1418.248		
Σ 1 0 <sup>o</sup> 0	2064.35	e	1.425220	-0.010028	3e 2064.208	4e 2067.061	5e 2072.765	0.14	-0.001
Π 0 3 <sup>o</sup> 0						5e 2113.413	6e 2119.150		
						2f 2113.453	3f 2119.272		
Π 1 1 <sup>o</sup> 0	2773.65	e	1.425332	-0.009916		6e 2775.458	7e 2781.155	-0.38	0.001
		f	1.432404	-0.002844		3f 2775.475	4f 2781.207		-0.001
Σ 0 0 <sup>o</sup> 1	3310.09	e	1.425220	-0.010028	5e 3309.089	8e 3311.939	10e 3317.639	1.00	0.000
Σ 0 0 <sup>o</sup> 2	6516.50	e	1.414943	-0.020305	17e 6515.669	30e 6518.498	40e 6524.155	0.83	0.001
Σ 0 0 <sup>o</sup> 3	9621.74	e	1.404360	-0.030888	41e 9621.550	75e 9624.357	104e 9629.971	0.19	0.001
Σ 0 0 <sup>o</sup> 0	0.00	e	1.207751	0.000000	1e 0.000	1e 2.416	1e 7.249	0.00	0.000
Π 0 1 <sup>o</sup> 0	570.26	e	1.208967	0.001216		2e 571.638	2e 576.465	-0.18	0.002
		f	1.215179	0.007428		1f 571.654	1f 576.516		0.000
Σ 0 2 <sup>o</sup> 0	1129.99	e	1.216650	0.008899	2e 1130.403	3e 1132.840	3e 1137.712	-0.41	-0.001
Δ 0 2 <sup>o</sup> 0	1142.77	ef	1.216264	0.008513			4e 1145.417	-0.22	
							2f 1145.417		
Π 0 3 <sup>o</sup> 0	1691.24	e	1.217916	0.010165		4e 1693.810	5e 1698.655	-1.36	0.007
		f	1.224284	0.016533		2f 1693.842	3f 1698.754		-0.004
Φ 0 3 <sup>o</sup> 0	1717.54	ef	1.220370	0.012619					
Σ 1 0 <sup>o</sup> 0	1925.27	e	1.201201	-0.006550	3e 1925.186	5e 1927.589	6e 1932.395	0.08	0.000
Π 1 1 <sup>o</sup> 0	2498.35	e	1.202128	-0.005623		7e 2499.634	9e 2504.437	-0.09	0.001
		f	1.208511	0.000760		3f 2499.650	5f 2504.485		0.000
Σ 0 0 <sup>o</sup> 1	2630.31	ef	1.197413	-0.010338	5e 2628.681	8e 2631.075	10e 2635.863	1.62	0.000
Σ 1 2 <sup>o</sup> 0	3060.68	e	1.209659	0.001908	6e 3060.846	10e 3063.269	12e 3068.114	-0.17	-0.002
Δ 1 2 <sup>o</sup> 0	3073.47	ef	1.209305	0.001554			13e 3075.963	-0.07	
							7f 3075.963		
Π 0 1 <sup>o</sup> 1	3184.87	e	1.198996	-0.008755		11e 3184.934	14e 3189.728	1.13	0.001
		f	1.205047	-0.002704		5f 3184.946	8f 3189.764		0.000
Π 1 3 <sup>o</sup> 0	3625.16	ef	not obs			13e 3626.438	17e 3631.258	-0.05	
						6f 3626.471	10f 3631.356		
Σ 0 2 <sup>o</sup> 1	3729.14	e	1.206942	-0.000809	8e 3728.542	14e 3730.954	18e 3735.779	0.60	0.001
Δ 0 2 <sup>o</sup> 1	3741.72	ef	1.206561	-0.001190			19e 3743.369	0.76	
							11f 3743.369		

Table 4. (cont.)

assignment	DCN 2-12-14, observed data/cm <sup>-1</sup>			calculated data/cm <sup>-1</sup>			obs-calc		
	$G(v)$	sym	$B(\text{eff})$	$\Delta(B)$	$J = 0$	$J = 1$	$J = 2$	$G(v)$	$B(v)$
$\Sigma$ 2 <sup>0</sup> 0	3836.35	e	1.194120	-0.013631	9e 3836.499	15e 3838.889	20e 3843.669	-0.15	-0.001
$\Pi$ 2 <sup>1</sup> 0	4412.18	e	1.195206	-0.012545		19e 4413.636	25e 4418.412	-0.27	0.001
$\Sigma$ 1 <sup>0</sup> 1	4523.27	e	1.201862	-0.005889		9f 4413.652	15f 4418.460		0.000
$\Pi$ 1 <sup>1</sup> 1	5080.66	e	1.191141	-0.016610	12e 4521.177	21e 4523.558	28e 4528.322	2.10	0.000
$\Sigma$ 0 <sup>0</sup> 2	5220.24	e	1.198782	-0.015179		26e 5080.232	35e 5085.000	1.62	0.001
$\Pi$ 0 <sup>1</sup> 2	5759.08	ef	1.187056	-0.008969	15e 5217.701	12f 5080.245	21f 5085.038	2.54	0.000
			not obs	-0.020695		27e 5220.074	36e 5224.820	-0.75	0.001
						34e 5758.635	40e 5763.390		
						15f 5758.646	27f 5763.423		

vibrational basis set at somewhere around  $v_2 = 24$ , so that our calculations will be lacking some high bending states above  $10000 \text{ cm}^{-1}$ , but it seems unlikely that this would significantly affect our calculation of the high energy stretching states listed in table 4.)

From trial calculations in which we have varied the size of the basis set we believe that in the final calculations reported below all of the eigenvalues are converged to within  $1 \text{ cm}^{-1}$  (i.e. errors in our calculation of the eigenvalues due to limitations of the basis set are all less than  $1 \text{ cm}^{-1}$ ), and we believe the lower eigenvalues are converged to within  $0.1 \text{ cm}^{-1}$ . Furthermore we believe that differences between  $J = 0, 1$  and  $2$  for the same vibrational state (corresponding to the rotational constant  $B$  in the particular vibrational state) are converged within  $0.002 \text{ cm}^{-1}$ . It is to be expected that such differences will be more accurately calculated than the absolute energies, because they are sensitive to terms in the hamiltonian representing rotational effects but relatively insensitive to the vibrational energy terms. Similar comments apply to our calculation of parity doubling effects ( $l$  doubling and  $l$  resonance, i.e. the splitting of e from f levels of the same  $J$  and  $|k|$  within the same vibrational state).

We have, finally, enclosed the entire calculation within a least squares procedure to refine the parameters (or a selection of parameters) in the potential to fit the observed energy levels. However, these calculations are computer-intensive, even before we build them into a least squares refinement procedure. The logistical limitations have so far restricted us to refining the potential to fit only the  $J = 0$  eigenvalues for a single isotopic species (the parent HCN molecule, with mass numbers 1-12-14). However, we carry out the forwards calculation from an assumed potential to eigenvalues and eigenfunctions for  $J = 0, 1$  and  $2$  for all the isotopic species on which data have been reported.

### 3. Results

The results of our calculations are shown in tables 1–4. Table 1 gives the parameters that define our final refined potential surface; table 2 gives parameters involved in setting up the basis functions; table 3 gives details of the dimensions of the basis sets; and table 4 gives a comparison between our calculated energy levels and those observed spectroscopically, all energies being expressed as vibration–rotation term values  $T$  referred to  $J = 0$  in the ground vibrational state for each isotopic species. The spectroscopic data are taken from Smith *et al.* (1989) and references found therein. The states are labelled with the customary quantum numbers  $(v_1, v_2', v_3)$ , where  $v_1$  is the excitation in the CN stretch,  $v_2'$  in the bend, and  $v_3$  in the CH stretch, in the customary (but illogical) spectroscopic convention. (This numbering is adopted in table 4 notwithstanding the different numbering of the internal coordinates adopted in §2 and in table 1 of this paper.)

For  $J = 0$  we calculate only  $\Sigma$  vibrational states; for  $J = 1$  we calculate  $\Sigma$  and  $\Pi$  states; and for  $J = 2$  we calculate  $\Sigma$ ,  $\Pi$  and  $\Delta$  states. Since we do not calculate states above  $J = 2$ , we do not calculate any vibrational states of symmetry  $\Phi$  or higher. The rotational constants are calculated as  $B = \frac{1}{4}\{T(J = 2) - T(J = 1)\}$  for  $\Sigma$  and  $\Pi$  states (we cannot calculate  $B$  for  $\Delta$  states without going to  $J = 3$ ). We could equally calculate  $B$  from the difference between  $J = 1$  and  $0$ , but the results are identical to within  $\pm 0.001 \text{ cm}^{-1}$ , and we do not believe our calculated term values are reliable to any higher precision. The term values in table 4 are given separately for the e and

f symmetry components of each  $\Pi$  and  $\Delta$  state; the difference gives the effective  $l$  doubling in the  $\Pi$  states. The final two columns of table 4 give the differences (observed – calculated) for the vibrational band origins and the rotational constants, respectively, for each vibrational state.

In the calculated term values shown in table 4, the eigenvalue number and symmetry label (e or f) are shown in the column immediately to the left of each calculated term value. Thus, for example, the  $\Sigma$  vibrational states at 17549.6 and 18376.5  $\text{cm}^{-1}$  are the 175th and 198th eigenvalues, respectively, from the  $J = 0$  matrix (of dimension  $701 \times 701$ ). In table 4 we have only quoted calculated values for the observed states, and for a few other unobserved states that we believe may be observed in the future, or are otherwise of interest. The vibrational assignments were made automatically in our program, by identifying the largest eigenvector element.

It is well known that the rotational structure and the vibrational energy levels contain complimentary information on the potential surface. The rotational constants themselves are most sensitive to the (equilibrium) molecular geometry, which is already well known for HCN (see table 2); however, the vibrational dependence of the rotational constants is sensitive to anharmonic effects. In the perturbation treatment of anharmonicity, the leading terms in the vibrational dependence of the rotational constants, the  $\alpha_r^B$  constants, relate to the cubic anharmonic force field. Since our present least-squares procedure is only able to refine to fit the  $J = 0$  energy levels, we chose to start from the potential surface reported by Strey & Mills (1973), determined from a perturbation calculation, for which the cubic anharmonic terms are already adjusted to reproduce the  $\alpha_r^B$  constants determined from the lower vibrational states. We have then refined the quartic and higher power terms in our potential surface, but we have not changed the quadratic and cubic terms from those reported by Strey & Mills. The potential constants that we have refined are marked in table 1. Table 4 shows that we calculate almost all of the rotational constants (and parity doubling splittings) for all isotopic species correct to  $\pm 0.001 \text{ cm}^{-1}$ . For vibrational states above 10000  $\text{cm}^{-1}$  this implies an accuracy of one part in  $10^7$ , but this accuracy probably only applies to differences between closely related eigenvalues rather than to their absolute values.

Table 4 also shows that we calculate most vibrational states of all isotopic species correct to within  $\pm 1 \text{ cm}^{-1}$ . The exceptions are almost all at high energy. (The 5.43  $\text{cm}^{-1}$  discrepancy for the (0, 2<sup>2</sup>, 1) state of the 1-13-14 species is probably due to an error in the spectroscopic data.) The well-known ( $\Delta v_1 = -3$ ,  $\Delta v_3 = +2$ ) resonance, between, for example, the levels at 14653 and 14671  $\text{cm}^{-1}$ , is successfully fitted. Apart from this example, the HCN overtone spectrum is actually remarkably free of anharmonic resonances. Thus both the vibrational energies and the rotational structure are fit with high accuracy, and the remaining discrepancies between our calculations and the observed data are more likely to be due to errors in our potential surface than to lack of convergence in our calculations. We believe that our potential surface is the most accurate surface yet produced for the HCN molecule over the range of coordinate space to which the spectroscopic data relate.

#### 4. Discussion

These results show that variational calculations for molecules like HCN can calculate vibrational and rotational structure up to high energy with high precision, and can be used to obtain a highly accurate potential surface. They relate the potential

surface directly to the spectrum for all isotopic species, and they incorporate all resonances (Fermi, Coriolis, Darling–Dennison, etc.) without special treatment. Wavefunctions are available (as linear combinations of the basis functions), and can be used to calculate transition intensities if the dipole moment surfaces are known; we are planning to do this for HCN in the near future. Similar calculations have been done by Jensen (1988*b*) for the CH<sub>2</sub> molecule, with great success. Reliable absolute intensity measurements are notoriously difficult to make experimentally, and it may well prove that the *ab initio* calculation of intensities by this method will prove to be an important technique.

However, variational calculations of rovibrational states have a number of limitations. A limitation of this work is that our results do not span the HNC minimum in the potential surface. The spectroscopic data on this molecule are confined to two well separated regions, one around the HCN minimum (going up to  $v_2 = 5$  and  $l_2 = 3$  in the bending mode), and one around the HNC minimum (where even less is known about excited bending states). The high precision and high quality fit of our calculation depends on using highly optimized basis functions, and it would be difficult to find such functions to span the whole of the HCN/HNC surface. Bačić & Light (1987) have in fact reported variational calculations on this molecule that range from the HCN to the HNC minimum, using a discrete variable representation (DVR) with a distributed gaussian basis (DGB). The DVR–DGB technique is well suited to non-rigid molecule problems that span a wide range of coordinate space, but it has not yet been used to obtain results approaching the precision of those reported here for HCN. In particular Bačić & Light's results span the full range of the bending coordinate from HCN to HNC, but they only span 1 quantum of excitation in each of the stretching coordinates.

The other main limitation of calculations of this kind is that they are computer intensive. The technique we are using will require a new program for almost every molecule. It requires substantial time on a super-computer, and even so it is hardly practical yet to go above  $J = 2$  for HCN, or to do a least squares refinement above  $J = 0$ . We are at present running a similar program for 4-atomic molecules, but full calculations over all the internal coordinates for larger molecules pose considerable problems. Nonetheless one should not underestimate the potential of variational calculations for treating the vibration–rotation problem. Recent developments in the formulation of these calculations, combined with developments in computer technology, have shown a far greater potential for applications of this method than appeared to be possible even five years ago.

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### References

- Aliev, M. & Watson, J. K. G. 1985 In *Molecular spectroscopy: modern research* (ed. K. N. Rao), vol. III, ch. 1. Academic Press.
- Amrein, A., Dübal, H. R. & Quack, M. 1985 *Molec. Phys.* **56**, 727.
- Bačić, Z. & Light, J. C. 1987 *J. chem. Phys.* **86**, 3065.
- Bačić, Z. & Light, J. C. 1989 *A. Rev. phys. Chem.* **40**, 469.
- Baggott, J. E., Clase, H. & Mills, I. M. 1986 *Spectrochim. Acta A* **42**, 319.
- Beyer, T. & Swinehart, D. F. 1973 *Commun. ACM* **16**, 379.
- Brown, J. M. *et al.* 1975 *J. molec. Spectrosc.* **55**, 500–503.

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- Burden, F. R. & Quiney, H. M. 1984 *Molec. Phys.* **53**, 917–927.
- Carney, G. D., Sprandel, L. L. & Kern, C. W. 1978 *Adv. chem. Phys.* **37**, 305.
- Carter, S. & Handy, N. C. 1982 *Molec. Phys.* **47**, 1445–1455.
- Carter, S. & Handy, N. C. 1986a *Molec. Phys.* **57**, 175–185.
- Carter, S. & Handy, N. C. 1986b *Comp. Phys. Repts* **5**, 117–171.
- Carter, S., Handy, N. C. & Sutcliffe, B. T. 1983 *Molec. Phys.* **49**, 745–748.
- Champion, J. P., Robiette, A. G., Mills, I. M. & Graner, G. 1982 *J. molec. Spectrosc.* **96**, 422–441.
- Child, M. S. & Lawton, R. T. 1981 *Faraday Discuss. chem. Soc.* **71**, 273.
- Child, M. S. & Halonen, L. 1984 *Adv. chem. Phys.* **57**, 1.
- Dübal, H.-R. & Quack, M. 1984 *J. chem. Phys.* **81**, 3779.
- Golub, G. H. & Welsch, J. H. 1969 *Math. Comp.* **23**, 221.
- Halonen, L. & Child, M. S. 1982 *Molec. Phys.* **46**, 239–255.
- Halonen, L. 1989 *J. phys. Chem.* **93**, 3386.
- Halonen, L. & Child, M. S. 1988 *Comp. Phys. Comm.* **51**, 173–193.
- Halonen, L., Kauppinen, J. & Caldow, G. L. 1984 *J. chem. Phys.* **81**, 2257.
- Handy, N. C. 1987 *Molec. Phys.* **61**, 207–223.
- Harris, D. O., Engerholm, D. O. & Gwinn, W. 1965 *J. chem. Phys.* **43**, 1515.
- Hoy, A. R., Mills, I. M. & Strey, G. 1972 *Molec. Phys.* **24**, 1265–1290.
- Jensen, P. 1983 *Comp. Phys. Rep.* **1**, 1.
- Jensen, P. 1988a *J. chem. Soc. Faraday Trans. II* **84**, 1315.
- Jensen, P. 1988b *J. molec. Spectrosc.* **132**, 429–457.
- Jensen, P. 1989 *J. molec. Spectrosc.* **133**, 438–460.
- MacDonald, J. K. L. 1933 *Phys. Rev.* **43**, 830.
- Mills, I. M. 1972 In *Molecular spectroscopy: modern research* (ed. K. N. Rao & C. W. Mathews), ch. 3.2. Academic Press.
- Mills, I. M. & Robiette, A. G. 1985 *Molec. Phys.* **56**, 743.
- Nielsen, H. H. 1951 *Rev. Mod. Phys.* **23**, 90.
- Papousek, D. & Aliev, M. R. 1982 *Molecular vibrational–rotational spectra*. Prague: Academia.
- Schwenke, D. W. & Truhlar, D. G. 1984 *Comp. Phys. Commun* **34**, 57.
- Senekowitsch, J., Carter, S., Zileh, A., Werner, H.-J., Handy, N. C. & Rosmus, P. 1989 *J. chem. Phys.* **90**, 783–794.
- Smith, A. M., Coy, S. L., Klemperer, W. & Lehmann, K. K. 1989 *J. molec. Spectrosc.* **134**, 134.
- Stein, S. E. & Rabinovitch, B. S. 1973 *J. chem. Phys.* **58**, 1301.
- Strey, G. & Mills, I. M. 1973 *Molec. Phys.* **26**, 129–138.
- Sutcliffe, B. T. 1982 In *Current aspects of quantum chemistry* (ed. R. Carbo). Amsterdam: Elsevier.
- Tennyson, J. & Sutcliffe, B. T. 1982 *J. chem. Phys.* **77**, 4061.
- Watson, J. K. G. 1968 *Molec. Phys.* **15**, 479.
- Watson, J. K. G. 1970 *Molec. Phys.* **19**, 465.
- Whitehead, R. J. & Handy, N. C. 1975 *J. molec. Spectrosc.* **55**, 356.
- Wilson, E. B. 1939 *J. chem. Phys.* **7**, 1047.
- Wilson, E. B. 1941 *J. chem. Phys.* **9**, 76.
- Wilson, E. B., Decius, J. C. & Cross, P. 1955 *Molecular vibrations*. McGraw Hill.
- Zare, R. N. 1988 *Angular momentum*. New York: Wiley.

### Discussion

N. C. HANDY (*Cambridge University, U.K.*). The calculation of rovibrational energy levels by the variational method has made tremendous progress since the first such calculations on triatomic molecules in 1975 (Carney & Kern 1975; Whitehead & Phil. Trans. R. Soc. Lond. A (1990)

Handy 1975). One of the first successes was the recognition that an expansion of the potential in powers of  $\Delta r$  through fourth order was not satisfactory; a much better representation is obtained by replacing  $\Delta r$  by the Simons–Parr–Finlan coordinate ( $\Delta r/r$ ), or the Morse coordinate ( $1 - e^{-\alpha\Delta r}$ ).

The question arises as to how one is to interpret the mass of data (many eigenvalues, each with a very long eigenvector) from such calculations. I like to consider the variational method as a theoretical spectrometer, which produces data on energy level differences in the same way as the experimental spectroscopist. One way therefore to analyse the output of the theoretical spectrometer is to do the same analysis as the experimentalist, that is to set up effective hamiltonians, etc. If such an analysis is successful, then such a model is realistic. If it is not, then the effective hamiltonian model is deficient. Finally, I would like to suggest that many of the levels that are calculated at high energy, but which are not observed in the spectrum, may correspond to ‘chaotic’ quantum states.

I. M. MILLS. I completely agree with Dr Handy’s remarks, particularly with his last comment about chaotic states. I also believe that most of these states may never be observed, due to the lack of an appropriate transition moment.

*Additional reference*

Carney, G. D. & Kern, C. W. 1975 *Int. J. Quant. chem. Symp.* **9**, 317.