Variational calculation of the rotational constants for acetylene and its isotopic derivatives\textsuperscript{a)}

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A method is presented for calculation of rotational constants for a linear molecule by treating the vibrations variationally, but treating the vibration–rotation coupling perturbatively. The method is applied to the potential energy function for acetylene given by L. Halonen, M. S. Child, and S. Carter [Mol. Phys. 47, 1097 (1982)]. It is found that even though the vibrational energy levels calculated from this potential are in excellent agreement with experiment, the calculated rotational constants are poorly predicted. The calculated \( \Delta B \)'s are systematically inaccurate by about 5% for C\(_2\)H\(_2\) and 8% for C\(_2\)D\(_2\). This indicates that the potential energy function is inaccurate even near equilibrium.

INTRODUCTION

Recent experimental work has generated a renewed interest in the properties of highly excited vibrational states.\textsuperscript{1,2,3} The traditional perturbation expansions are expected to converge slowly,\textsuperscript{4} if at all, for highly excited states, making other methods of calculation desirable. Variational techniques offer a powerful method for calculation of even highly anharmonic energy levels.\textsuperscript{5}

In a recent article,\textsuperscript{6} Halonen, Carter, and Child used variational techniques to fit a potential energy function with four free parameters for linear acetylene. They fit the observed vibrational energy levels of both C\(_2\)H\(_2\) and C\(_2\)D\(_2\) to separate potential functions. The standard deviation of the fits was 6 and 3 cm\(^{-1}\), respectively, which is exceptionally good for the simple function chosen. In addition, the potentials gave accurate predictions when extended to other isotopes,\textsuperscript{7} and higher levels of excitation than those that were included in the fit. The bending degrees of freedom were neglected, but the good fit, as well as close agreement of the C\(_2\)H\(_2\) and C\(_2\)D\(_2\) potentials, argues strongly that only small errors are introduced by this approximation. Based upon experimental values for the anharmonic constants of C\(_2\)H\(_2\) and C\(_2\)D\(_2\),\textsuperscript{8} we can estimate that the errors introduced by this approximation are on the order of 1%.

One conclusion of that work was that the energy level spacings of C\(_2\)D\(_2\) are close to that expected from the normal mode approximation, while C\(_2\)H\(_2\) has many pairs of levels, more indicative of local mode behavior. This is in agreement with an earlier, qualitative calculation by Child and Lawton.\textsuperscript{9} That work showed the transition expected as an \( X_2 Y_2 \) molecule goes from normal to local mode behavior. It was found that C\(_2\)D\(_2\) is relatively close to the normal mode limit, but that C\(_2\)H\(_2\) is nearly halfway between the two extremes. In spite of this, the most anharmonic levels showed pairing of levels whose splitting decreased with increasing excitation. This decreasing splitting has been interpreted as evidence that these quantum states are close to the eigenfunctions of an uncoupled local mode Hamiltonian.\textsuperscript{10} Given the fact that C\(_2\)H\(_2\) is predicted to be nearly halfway between normal and local mode limits, it is possible that these splittings merely give an illusion of local mode behavior. It is possible to obtain the energy level pattern of C\(_2\)H\(_2\) from a normal mode, anharmonic expansion if Darling–Dennison\textsuperscript{11} resonance interactions are included.\textsuperscript{12}

It is well known that the calculated energy of a state is insensitive to errors in the trial wave function.\textsuperscript{13} We believe that it is important to include other operators in any comparison of variational calculations to experiment. Since high resolution spectroscopy has produced accurate rotational constants for the excited vibrational states of acetylene, we decided to extend the variational calculations to include the vibrational dependence of \( B \). This calculation reveals shortcomings in the potential functions of Ref. 6, despite their success at predicting vibrational energy levels of acetylene isotopes. Because the predicted \( \Delta B \)'s are in error by more than \( B \) changes on going from normal to local mode motion, the calculations cannot be used as a test of the character of the vibrational state, as it was hoped they would.

Because of the local mode appearances of its vibrational spacings, C\(_2\)H\(_2\) states will be labeled by local mode quantum numbers \((n, v_2, m)\), where \( v_2 \) is the C–C quantum number, and we have \( m \) quanta of excitation in one local mode, \( n \leq m \) in the other, and states have been symmetrized (+) or antisymmetrized (−). Our notation is different from that of Ref. 6, because we want the transition from local to normal mode quantum numbers to be as smooth as possible. In addition, this notation stays as close to the standard notation of Herzberg\textsuperscript{14} as possible. This notation was used in our previous experimental paper on the overtones of acetylene.\textsuperscript{2} The C\(_2\)D\(_2\) states will be labeled by normal mode notation, with \( v_2 \) the C–C stretch, \( v_1 \) the symmetric C–D stretch, and \( v_3 \) the antisymmetric stretch. The local mode states \((n, v_2, m)\) correlate to \((2n, v_2, m – n)\) in the normal mode limit. The local mode states \((n, v_2, m)\) correlate to \((2n + 1, v_2, m – n – 1)\) in the normal mode limit. This correlation is a consequence of the antisymmetric stretch being lower in energy than the symmetric C–H stretch. Though this is how the local mode levels correlate as the intrabond coupling is raised, it is not the normal mode assignment one gets if one views the levels as anharmonic normal modes with Darling–

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CALCULATION OF VIBRATIONAL PROPERTIES

Acetylene was treated as a linear molecule, with masses and coordinates given in Fig. 1. In our calculation, we used the potentials for C_2H_2 and C_2D_2 given in Ref. 6.

\[ V(r_1, r_2, r_3) = \sum_{i=1}^{3} D[1 - \exp(-\alpha r_i)^2] + \frac{1}{6} k_{2222} r_2^2 + \frac{1}{2} k_{2222} r_2^4 + \frac{1}{2} k_{12} r_1 r_2 + \frac{1}{2} k_{23} r_2 r_3, \]

(1)

where \( r_1 \) and \( r_2 \) are displacements of the C–H(D) bonds, and \( r_3 \) is the displacement of the C–C bond. The parameters for the potentials for C_2H_2 and C_2D_2 are given in Table I, together with a comparison to the anharmonic force field of Strey and Mills. In this table, indices 1 and 3 can be interchanged due to the symmetry of the molecule. The force constants \( k_{2222} \) and \( k_{12} \) were constrained in the fit to the values given by Strey and Mills. The force constant \( k_{23} \) was not found to be significantly different from these values.

The agreement between the vibrational potentials and the anharmonic force field is quite good for the diagonal force constants, but surprisingly different for the off-diagonal force constant \( k_{12} \). According to Halonen, when a fit was made to experimental energies corrected for bend–stretch anharmonicity the \( k_{12} \) obtained was close to that of Strey and Mills. Because the bending degrees of freedom were neglected in the variational calculation, the resulting potential represents an average over the bending zero point motion. The small differences between the C_2H_2 and C_2D_2 potentials were attributed to differences in the effective stretching potential, due to averages over different bending amplitudes.

The Hamiltonian for linear acetylene can be written as

\[ H = H_0(p_1, p_2, r_1, r_2, r_3) + H_{12}(p_1, p_2, r_1, r_2, r_3) + H_{23}(p_2, r_2, r_3) + H_{123}(p_1, p_2, p_3, r_1, r_2, r_3), \]

(2)

where

\[ H_i = \frac{\hbar^2}{2\mu_i} + D[1 - \exp(-\alpha r_i)^2], \]

(3)

where \( i = 1 \) or \( i = 3 \), and

**Acetylene Coordinates**

<table>
<thead>
<tr>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>m_1</td>
<td>m_2</td>
<td>m_3</td>
</tr>
</tbody>
</table>

**FIG. 1.** Masses and coordinates of linear acetylene.

### TABLE I. Comparison of potential derivatives.

<table>
<thead>
<tr>
<th>( k_{ij} )</th>
<th>( C_2H_2 )</th>
<th>( C_2D_2 )</th>
<th>Strey and Mills</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{11} )</td>
<td>6.33076(841)</td>
<td>6.34869(416)</td>
<td>6.370(10)</td>
</tr>
<tr>
<td>( k_{12} )</td>
<td>-0.0304(151)</td>
<td>-0.03059(47)</td>
<td>-0.095(10)</td>
</tr>
<tr>
<td>( k_{22} )</td>
<td>16.048(437)</td>
<td>16.1515(72)</td>
<td>16.341(50)</td>
</tr>
<tr>
<td>( k_{13} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( k_{111} )</td>
<td>-33.021(89)</td>
<td>-33.331(8)</td>
<td>-34.821(90)</td>
</tr>
<tr>
<td>( k_{112} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.002(21)</td>
</tr>
<tr>
<td>( k_{121} )</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.36(47)</td>
</tr>
<tr>
<td>( k_{122} )</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.50(84)</td>
</tr>
<tr>
<td>( k_{131} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.71(129)</td>
</tr>
<tr>
<td>( k_{132} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.71(129)</td>
</tr>
</tbody>
</table>

4Uncertainties are one standard deviation in last place. Values without errors were constrained in fit.

Our calculations were done by diagonalizing each of the one dimensional, local mode Hamiltonians in a basis of 75 harmonic oscillator functions and then transforming the operators \( r_i, r_i^2 \), and \( p \) to the eigenvector basis. The full Hamiltonian was then diagonalized using a basis set of products of the local mode wave functions. Symmetrized basis functions were not used because we wanted to study the nonsymmetric isotopes.

Calculations on C_2H_2 were done with a basis set consisting of all states with \( n + m \leq 10 \) and \( \nu_2 \leq 4 \). Comparison of our results with Ref. 6 reveals that our eigenvalues are slightly more converged for states with \( \nu_2 = 0 \), but slightly less converged for states with \( \nu_2 = 1, 2 \). The size of the basis set used in Ref. 6 was not noted, but recently Halonen has informed us that it was all states with \( n + m \leq 9 \) and ten harmonic oscillator functions for \( \nu_2 \).

Our results were checked for convergence by evaluating the perturbation corrections to the energy from all remaining states with \( n + m \leq 15 \) and \( \nu_2 \leq 10 \). This calculation showed that for states at \( \approx 150 \) cm\(^{-1}\) above the ground state, the levels assigned \( \nu_2 = 0 \) are converged to \( \approx 0.05 \) cm\(^{-1}\), those with \( \nu_2 = 1 \), \( \approx 1 \) cm\(^{-1}\), while those with \( \nu_2 > 1 \) are erratic. Since almost all of the observed states have \( \nu_2 = 0 \), this is not a serious problem. The highest observed level with \( \nu_2 = 2 \) (0, 2, 4') is converged to \( \approx 6 \) cm\(^{-1}\). There is one difficulty with this lack of convergence. The levels (0, 0, 6') are in Fermi resonance with other levels with \( \nu_2 = 3 \). This Fermi resonance disappears when more \( \nu_2 \) functions are included.

Because of the extensive mixing of the C–D and C–C
modes in $C_2D_2$, calculations on that isotope were done with a local mode basis set of all levels with $v_2 \leq 7$ and $n + m \leq 7$. Levels with five quanta of $C$--$D$ vibration are converged to better than 1 cm$^{-1}$. The calculations for the $^{13}C$ isotopes were done using the $C_2H_4$ potential with no adjustments. The same size basis set was used. The isotope $C_2HD$ was done using the $C$--$H$ bond potential from $C_2H_4$ and the $C$--$D$ bond potential from $C_2D_2$. C--C force constants came from the $C_2D_2$ potential, as that gave a better agreement with the fundamental frequencies. The basis set consisted of all states with $v_1 + v_3 \leq 9$ and $v_2 \leq 5$. Halonen, Noid, and Child$^t$ treated $C_2HD$ using the $C_2D_2$ potential for the entire molecule. Our choice of potential does significantly better at predicting the fundamentals and low lying overtones. For the asymmetric isotopic species, Halonen, Noid, and Child used a basis set of all functions with $v_1 + v_3 \leq 10$ and $v_2 \leq 10$.

CALCULATION OF ROTATIONAL CONSTANTS

Rotational constants are more sensitive indicators of the coupling between the $C$--$H$ oscillators in $C_2H_4$ than the vibrational energy. This is illustrated by the fact that $\alpha_3 - \alpha_2/\alpha_1 = 0.121$ but $\nu_3 - \nu_2/\nu_1 = 0.023$. This is countered by the fact that vibrational energy intervals are measured more precisely than changes in rotational constants. However, analysis of high resolution spectra of acetylene has produced measured changes in $B$ to a fractional accuracy of $\approx 10^4$. This is the level of accuracy to which the variational calculations can fit the observed vibrational term values. These rotational constant measurements can be used as sensitive tests of the nature of the vibrational wave functions, if accurate constants can be calculated for comparison.

Previous workers have calculated rotational constants variationally. They have done so by calculating the energy of $J = 0$ and $J = 1$. Because the change in $B$ can be measured to an accuracy of $10^{-9}$ of a vibrational term value, this method will be inaccurate due to round-off error, lack of convergence of the vibrational energies that is orders of magnitude times larger, and errors in integration if numerical integration is used. In addition, the size of the matrices to be diagonalized grows as $2J + 1$ (the number of values of $I$ that couple), and so greatly restricts the number of vibrational functions that can be used in the calculation. Rotational constants are in fact the coefficients of a perturbation expansion in powers of $J(J + 1)$. As long as this expansion is rapidly convergent, which is an experimentally determinable question, we believe that it makes more sense to calculate the vibrational dependence of the rotational constants by treating the vibration-rotation interaction terms of the Hamiltonian as perturbations, with the matrix elements given by the variational wave functions.

THEORY

Watson$^{17}$ showed that the Hamiltonian for a linear molecule can be transformed to Hugen's$^{28}$ isomorphic Hamiltonian given by

$$ H = \frac{\hbar^2}{2} \sum Q_i^2 + V(Q_i) + \frac{\hbar^2}{2} \mu \left[ (J_x - G_x)^2 + (J_y - G_y)^2 \right] $$

with $Q_i$, $P_i$ the mass weighted Cartesian displacements and their conjugate momenta; $V(Q)$ the potential energy; $G_x$ the vibrational angular momenta; $J_q$ the total angular momenta, $x, y$ body fixed coordinates perpendicular to the molecular axis; and $\mu$ the inverse of the effective moment of inertia operator, $\mu$ is given by

$$ \mu = (I')^{-1} = I_0^2 (I''')^{-2}, $$

where $I_0$ is the equilibrium moment of inertia and $I'''$ is given exactly by:

$$ I''' = I_0 + \frac{1}{2} \sum q \sqrt{a_0 q}, $$

$$ a_0 = \frac{\partial I_{0}}{\partial Q_0}. $$

where $q$ is the derivative of the moment of inertia with respect to coordinate $Q_0$. It was calculated by the expression given by Watson.$^{17}$

Because $I_q$ the moment of inertia operator, must be fully symmetric, $a_0 = 0$ unless $Q_0$ belongs to the totally symmetric representation. Therefore, $\mu$ is independent of nontotally symmetric vibrations. This is an unexpected result, for the moment of inertia operator does depend upon products $Q_i Q_j$, as long as the product is totally symmetric.

We can cast the rotational term in a more useful form by introducing raising and lowering operators of $J$ and $G$

$$ J_i = \{ J_x \pm i J_y \}, $$

$$ G_i = \{ G_x \pm i G_y \}. $$

The sign for the $J_i$ operator is opposite the usual one because of the different commutation relations for body fixed $J$. Vibrational angular momenta obey the conventional, space fixed relations. Using $J_z^2 + J_x^2 = J_y^2 + J_z^2$ we get that the last term in $H$ [Eq. (6)] may be written

$$ \frac{\hbar^2}{2} \mu \left[ J_x^2 - J_y^2 - J_z G_x - J_z G_y + \frac{1}{2} (G_x G_y + G_y G_x) \right]. $$

The term $G_x G_y + G_y G_x$ has no $J$ dependence and only connects states of the same $I$, and so affects only the vibrational energy, not the rotational energy. Since $G \neq P Q_i$, this term is of fourth power and has an effect similar to bend--stretch fourth order force constants. Therefore, it does not enter into a calculation of $B$, and will be dropped. We note that it was not included in our variational calculation of linear acetylene. We can write the rotational energy operator (the remainder of expression 11) as

$$ \mu_{x} \mu_{y} \left[ (J_x^2 - J_y^2) + \frac{1}{2} \mu \left[ (J_x^2 - J_y^2) \right] \right] $$

$$ - \frac{\mu_{x}}{2} \left[ J_x G_x + J_y G_y \right] - \frac{\mu_{y}}{2} \left[ J_y G_y + J_x G_x \right]. $$

We have introduced $\mu_{x} = I_{0x}^2$ in order to split terms of different order. If we look at the magnitude of the terms we find that: (1) The first is diagonal in vibrational coordinate, and has eigenvalues $B_{qq}(J(J+1) - 1)$. This is just the rigid rotor contribution. (2) The second has terms both diagonal and off diagonal in vibration, with the magnitude of the diagonal terms $= (2E_{0})^2(\omega)J(J+1)$, where $\omega$ is a vibrational energy. The off-diagonal terms contribute to the distortion constants through second or-
der in perturbation. This term contains the vibrational dependence of the average of the inverse effective momentum of inertia operator, and therefore represents changes in geometry with vibrational excitation. (3) The third term is off-diagonal in vibration, and only connects states differing by \( \Delta \ell = \pm 1 \). The magnitude of the matrix elements are \( B_{\ell} \Delta \ell \langle \ell | \partial \rangle \). \( \langle \ell | \partial \rangle - \hbar \) for an allowed coupling, so the matrix elements are of magnitude \( B_{\ell} \Delta \ell \). Their contribution to second order is of order \( (B_{\ell}^2/\omega) \Delta \ell \), and is, therefore, of comparable magnitude of the earlier term. This term is responsible for Coriolis coupling of vibrational states. These two terms contribute to the \( \varphi_{\ell} \)'s in the usual perturbation treatments. (4) The last term is smaller than term 3 by about the same factor that term 2 is smaller than term 1. It will be neglected since its contribution is of the next order in perturbation theory. If the agreement between calculation and experiment had been better, we would have included this term, but its contribution is believed to be smaller than the residual errors. Including it would have prevented overlying of some arrays, and required an addition nested sum over states.

**CALCULATION OF MATRIX ELEMENTS**

One can calculate a transformation from the \( Q \)'s to the \( r \)'s, the bond displacements. The \( Q \)'s can be any orthogonal internal coordinates that obey the Eckart\(^{(5)}\) conditions. When bending coordinates are neglected, this transformation is linear and is written as

\[
Q_{\ell} = \sum_{j} L_{jk}^\ell r_{j} .
\]

The conjugate momenta will be related by

\[
P_{\ell} = \sum_{j} L_{jk}^\ell \dot{p}_{j} .
\]

Here \( L \) is not unitary, because the \( r_{j} \)'s are not orthogonal. The effective momentum of inertia operator can be written as

\[
I' = I_0 + \sum b_{h} r_{h} + \sum_{lm} b_{lm} \lambda_{lm} r_{l} r_{m} ,
\]

where

\[
b_{lm} = \sum_{h} a_{h} \lambda_{h} .
\]

Therefore, the matrix elements of \( I' \) are easily calculated given the matrix elements for \( r_{j} \) and \( r_{j}^2 \), and the transformation \( L \). The matrix elements of \( \mu \) can be calculated by inverting the matrix \( I' \).

The vibrational angular momentum operator \( G \) is given by

\[
G_{\ell} = \sum_{lm} L_{km}^\ell r_{k} P_{m} .
\]

The \( r_{k} \)'s are the Coriolis coupling constants, connecting vibrational coordinates \( Q_{k} \) with \( Q_{m} \) by rotation about the \( \alpha \) molecular axis. They are given by Watson.\(^{(11)}\) For a linear molecule, the \( Q \)'s can be split into \( Q_{x} \) for stretching vibrations, \( Q_{y} \) for \( x \)-polarized bending vibrations, and \( Q_{z} \) for \( y \)-polarized bending vibrations. The only nonzero terms in \( \xi^{x,y} \) are

\[
\xi^{x,y} = -\xi^{y,x} = \xi^{x} .
\]

If we define

\[
Q_{\ell} = 2^{-1/2} \left[ \left( \xi_{\ell} \pm i \zeta_{\ell} \right) \right] ,
\]

\[
P_{\ell} = 2^{-1/2} \left[ \left( \xi_{\ell} \pm i \zeta_{\ell} \right) \right] ,
\]

it follows, after substituting Eqs. (17), (18), and (19) into Eqs. (10), that

\[
\xi_{\ell} = \sum_{t} \pm i^{2 \ell+1} \xi_{t} \left( Q_{t} P_{\ell} - P_{\ell} Q_{t} \right) .
\]

To proceed further, we must decide how to treat the bending coordinates. We will treat the bends as harmonic oscillators. The bending force constants were taken from the force field of Strey and Mills.\(^{(9)}\) We define creation operators for the bending normal modes by

\[
a_{t}^{\dagger} = 2^{-1/2} \left[ a_{t}^{\dagger} + i \beta_{t} \right] .
\]

The creation operator \( a_{t}^{\dagger} \) will add one quantum to the \( t \)'th vibrational mode, adding one unit of vibrational angular momentum about the \( z \) axis. The creation operator \( a_{t}^{\dagger} \) will subtract one unit of vibrational angular momentum about \( z \). Using \( \beta_{t} = (\omega_{t}/\hbar)^{1/2} \) and the usual expressions for \( Q_{t} \) and \( P_{t} \) in terms of the creation and annihilation operators we get

\[
G_{t} = \sum_{t} S_{t} a_{t}^{\dagger} - S_{t} a_{t} ,
\]

where

\[
S_{t} = \hbar \beta_{t} \sum_{t} \xi_{s,t} r_{s} + \frac{1}{\beta_{t}} \sum_{t} \xi_{s,t} i P_{t} .
\]

The matrix elements of \( a_{t}^{\dagger} \) are

\[
\langle n+1 \mid a_{t}^{\dagger} \mid n \rangle = \left( \frac{n + 1}{2} \right)^{1/2} .
\]

All others are zero. By using \( L \), \( L^{-1} \) defined previously we get

\[
\sum_{t} \xi_{s,t} Q_{s} = \sum_{t} S_{t} r_{s},
\]

\[
\sum_{t} \xi_{s,t} P_{s} = \sum_{t} \xi_{s,t} r_{s} .
\]

We conclude that the matrix elements of \( S_{t} \) are easily calculated from the matrix elements of \( r_{j} \) and \( P_{j} \), using Eq. (25). The matrix elements of \( G_{t} \) are then calculated from \( S_{t} \) using Eq. (22). The matrix elements for \( G_{t} \) have \( \Delta \varphi_{\text{hewa}} = \pm 1 \) selection rules if we treat the bending coordinates with harmonic oscillator basis functions.

**CALCULATIONS**

Because the calculation of vibrational term values described earlier was so accurate despite neglect of the bending coordinates, rotational constants were first calculated without including the Coriolis contributions. The spectroscopic constants are then given as

\[
B_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle ,
\]

\[
D_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle ,
\]

\[
E_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
J_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
K_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
L_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
M_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
N_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
O_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
P_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
Q_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
R_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
S_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
T_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
U_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
V_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
W_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
X_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
Y_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]

\[
Z_{\nu} = \frac{\hbar^{2}}{2} \langle \nu | \mu | \nu \rangle .
\]
TABLE II. ¹²C₂D₂ rotational constants.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Obs.</th>
<th>Calc.</th>
<th>ΔB × 10⁹ cm⁻¹</th>
<th>Obs.</th>
<th>Calc.</th>
<th>From α'</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1764.796</td>
<td>1764.96</td>
<td>3.31(2)</td>
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<tr>
<td>001</td>
<td>2439.244</td>
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<tr>
<td>100</td>
<td>2705.160</td>
<td>2704.13</td>
<td>5.86(4)</td>
<td>5.74</td>
<td>5.86</td>
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</tr>
<tr>
<td>011</td>
<td>4190.64</td>
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<td>7.56(6)</td>
<td>6.89</td>
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<tr>
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<td>25.49</td>
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\[ D_\nu = -\frac{\hbar^2}{4} \sum_{\nu_0} \langle \nu | \mu | \nu \rangle^2 \frac{E_\nu - E_{\nu'}}{E_\nu} \]

The resulting calculation overestimates the observed ΔB's by ~50%. The calculated D for the ground state agrees well with experiment (D₀ observed is 1.598(9) × 10⁻⁹ cm⁻¹, ⁴⁵ while D₀ calculated was 1.5803 × 10⁻⁹ cm⁻¹) but the vibrational dependence of D was similarly poorly calculated.

The inclusion of contributions to B from the Coriolis interactions in second order is shown to be essential for even a qualitative agreement with experiment. The Coriolis contribution was calculated by second order perturbation theory. The intermediate levels for the perturbation expression are taken to be product functions of a stretching function calculated variationally, and a harmonic oscillator function for the bend. The energy of these states is assumed to be the sum of the energy of the stretching state and the harmonic energy for the bending vibrations. Because of the assumption of harmonic bending coordinates, the intermediate levels can only have one quantum of either of the bending normal coordinates. This is because G₄₅ is linear in the creation and annihilation operators of the bending modes. Removing the harmonic assumption would require summing over all bending levels with ±1 unit of vibrational angular momentum about the molecular axis. This perturbation calculation will be inaccurate if there is a strong resonance between a zero point bending level and one with bending excitations. Such a resonance occurs in the ν₃ fundamental of ¹²C₂H₂. However, experimentally it is known that most of the zero point bending levels are not in resonance, so this should be a good approximation for most of the zero point bending levels. The distortion constant was not calculated, as that would have required including the fourth order contributions.

At first it appears curious that the rotational constants are given so poorly from the stretch only calculation, while the vibrational energies are predicted so accurately. In part, the vibrational calculation gives effective potential constants to make up the bend/stretch interactions. As discussed previously, we believe that to be a minor effect. There is a simple physical explanation. For a linear molecule, the lowest order potential coupling between bending and stretching degrees of freedom must go as the bend angle squared. For unexcited bending levels, the contribution of these terms to the energy will be small. When a molecule rotates, the Coriolis interaction bends the molecule with a force that is proportional to the stretching velocity times the rotational angular velocity. This force has a significant impact on the dependence of the energy upon rotational quantum number. A recent calculation on H₂O²⁺ has shown that even the vibrational energy levels are poorly calculated if the Coriolis contribution to the vibrational Hamiltonian is neglected.

Comparison of the calculated ΔB's with experimental results are listed in Tables II–VI for the five isotopes that have been observed. The experimental values for C₂H₂ come from Refs. 2, 22, 23, 24, and 25, those for C₂D₂ from Refs. 2, 26, 27, 28, and 29, for C₂HD from Refs. 2, 25, 29, 30, and 31, for ¹⁴C₂H₂ and ¹²C₂H₂ from Refs. 2 and 30. The agreement, though qualitatively correct, is still disappointing. For comparison, the ΔB's predicted from the experimentally determined normal mode α's are listed for the most studied isotopes C₂H₂, C₂D₂, and C₂HD. The average percent error for both sets of ΔB's is shown in Table VII. In this average error the state (001') of C₂H₂ was not included since it is known to be in Fermi resonance with a bending level. Also, the level (012) of C₂HD was not included since the anomalously large discrepancy is due to an accidental Coriolis resonance in the calculation. Our calculation of bending level energies is too crude to accurately predict such a resonance. It is seen that the variationally calculated ΔB's do not do as well as the use of linear, normal mode α's. This is even true for C₂H₂ where the states are not even approximately normal modelike.

The percent errors do not increase rapidly as the
states energy increases, so we are confident that the discrepancy is not due to lack of convergence in the variational calculation. We also do not believe that the small anharmonicity of the bending vibrations can account for such a large disagreement. The agreement is worse for C\textsubscript{2}D\textsubscript{2} which has a smaller amplitude of bend than C\textsubscript{2}H\textsubscript{2}, yet if the error came from neglecting the anharmonicity of the bends, we would expect that C\textsubscript{2}H\textsubscript{2} would fit better.

We conclude that the potential energy function given in Ref. 6 is inaccurate, despite the exceptionally good fit it gave to the experimental vibrational energies. The reason for this paradox can be understood by looking at the end of Ref. 6. There it is shown that a modified version of Child and Lawton’s\textsuperscript{5} simple model can predict the vibrational energies to an accuracy equivalent to that of the variational calculation. Thus the vibrational energies are only sensitive to a small subset of the possible parameters in the potential.\textsuperscript{19} This behavior is well known in diatomic molecules.

We strongly urge that future fits of potentials by variational calculations be extended to fit rotational constants as well. This is in accord with the usual procedures of fitting anharmonic force fields by perturbative methods. If it is too difficult to calculate the rotational constants by the methods used here, it is probably ade-

<table>
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<tr>
<th>Assignment</th>
<th>Obs.</th>
<th>Calc.</th>
<th>$\Delta \beta \times 10^3$ cm$^{-2}$</th>
<th>Obs.</th>
<th>Calc.</th>
<th>From $\alpha$,</th>
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<td>36.76</td>
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J. Chem. Phys., Vol. 79, No. 3, 1 August 1983
quate to evaluate the $\alpha$'s by the usual perturbation formula. Table VIII lists a comparison of the $\alpha$'s calculated for the $C_2H_2$ potential with the calculated $\Delta B'$s for the three fundamentals. The error is seen to be $\sim 2.5\%$ for $C_2H_2$ and 1.3% for $C_2D_2$, indicating that the discrepancy is due to the anharmonicity of the $C$–$H$ bond. This provides the level of accuracy expected for the perturbation formula. They probably could be significantly improved by going beyond the first-order of the perturbation expansion and calculating the $\gamma$'s, the corrections to $B$ that depend upon the square of the vibrational quantum numbers. As an example consider the cubic force constants in the acetylene potential. If we use the perturbation formula and the harmonic part of the potentials in Ref. 6, we can relate the three observed $\alpha$'s, to the cubic force constants. There are six independent cubic force constants for linear acetylene, but if we set the off-diagonal constants to zero, we are left with two independent constants, $k_{111}$ and $k_{222}$. Fitting these two constants to the three $\alpha$'s gives $k_{111} = -34.86 \pm 0.10$ a.u.$^2$ and $k_{222} = -96.47 \pm 0.31$ a.u.$^2$ for the $C_2H_2$ diatomic and $k_{111} = -35.50 \pm 0.16$ a.u.$^2$ and $k_{222} = -93.75 \pm 1.38$ a.u.$^2$ for the $C_2D_2$ diatomic. Not surprisingly, the cubic constants are closer to those of Strey and Mills than those of the Morse potentials. That is, because the cubic constants of Ref. 8 come from a fit to the $\alpha$'s for five isotopes, though with a slightly different harmonic force field. The constants listed above agree to about the level expected based upon the comparisons of the variational calculation and the perturbation predictions. Therefore, we cannot say if the disagreement is due to neglect of the off-diagonal cubic force constants or not. The quartic force constants could be adjusted to give the correct vibrational frequencies, but it is clear they will not obey the relationship for a Morse potential. The C–H vibration will need to be parametrized by a more general potential than a Morse if an accurate potential is to be obtained. We do not have the computational resources to optimize to potential using both vibrational and rotational data.

**CONCLUSION**

We have shown how to calculate accurate rotational constants for a linear molecule from the variational wavefunctions. The method was applied to acetylene, with two observations. First, a substantial part of the vibrational dependence of the rotational constants is due to Coriolis interactions. This indicates that interpretations of the rotational constants only in terms of changes in average geometry are inaccurate. Second, the calculated rotational constants are disappointingly far from experimental observations. This indicates that the potential fitted by Halonen, Carter, and Child is less accurate than would appear based upon its success at fitting and predicting vibrational energies alone. We conclude that in the calculation of polyatomic potentials no experimental information should be ignored. In particular, rotational constants should always be calculated, even if only by perturbation theory. This is in accord with convention in anharmonic force field calculations. We also suggest that all couplings be given functional forms that dissociate properly, so that dissociation energies can be included in the fits. This is easily done in cases where bond potentials are described by Morse potentials by making the replacement $\Delta r_i - (1 - e^{-\alpha})/\alpha$, which has the same small displacement dependence.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Variational calculation $\alpha_i$</th>
<th>$\Delta B' \times 10^3$ cm$^{-1}$</th>
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<tr>
<td>$^{12}C_2H_2$</td>
<td>5.1%</td>
<td>4.2%</td>
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<tr>
<td>$^{12}C_2HD$</td>
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<td>6.0</td>
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<td>8.0</td>
<td>1.0</td>
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<td>$^{12}C_2D_i$</td>
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**TABLE VIII. Comparison of $\alpha_i$ and $\Delta B_i$ calculated for the acetylene Morse potential.**

<table>
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<tr>
<th>$i$</th>
<th>$\omega_i$</th>
<th>$\alpha_i \times 10^3$</th>
<th>$\Delta B_i \times 10^3$</th>
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<td>4.012</td>
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J. Chem. Phys., Vol. 79, No. 3, 1 August 1983

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TABLE V. $^{12}C^{13}CH_2$ rotational constants.

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<th>$G_i$ (v)</th>
<th>$\Delta B' \times 10^3$ cm$^{-1}$</th>
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TABLE VI. $^{12}C_2H_2$ rotational constants.

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ACKNOWLEDGMENTS

We would like to acknowledge the helpful comments on our manuscript given by Dr. Lauri Halonen and Dr. Mark Child.

15 L. Halonen (private communication).

J. Chem. Phys., Vol. 79, No. 3, 1 August 1983