

# Harmonically coupled, anharmonic oscillator model for the bending modes of acetylene

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The harmonically coupled anharmonic oscillator model developed by Child and co-workers is extended to treat the coupling of two doubly degenerate "local benders" as may be expected in acetylene. This effective Hamiltonian is transformed to the normal mode representation and a set of "x-K" relations derived that relate the anharmonic and Darling-Dennison-type resonance terms to the diagonal local bending anharmonic constant. It is found that these relations agree very poorly with the experimental constants determined by Pliva in a fit to the acetylene spectrum. This failure is attributed to a remarkable cancellation of cubic and quartic contributions to the constants.

The harmonically coupled, anharmonic oscillator (HCAO) model, introduced by Child and Lawton,<sup>1</sup> has been a highly successful model for studying the stretching vibrations of molecules with equivalent hydrogens.<sup>2</sup> It is now known that this model is exactly equivalent to a traditional normal mode, second order anharmonic expansion including Darling-Dennison resonance terms, if one imposes a set of relations between the anharmonic terms.<sup>3-7</sup> These conditions, named "x-K" relations by Ian Mills, hold reasonably well for constants used to fit spectra of simple hydrides, as well as for those calculated from model force fields.<sup>4</sup> In this letter, I will present a HCAO model for the two hydrogen bending vibrations of a  $D_{\infty h}$  molecule such as acetylene. It is found that the x-K relations predicted by this model do not even approximately reproduce the known anharmonic constants of acetylene. The difficulty is that the cubic and quartic contributions almost exactly cancel one another in the expressions for the bending anharmonic constants. While the x-K relations hold reasonably well for either the cubic or the quartic contributions, they work poorly for the sum.

Consider two doubly degenerate "local" bender modes of a molecule. The energy levels for each oscillator is given to second order as

$$E_{n,l} = \omega_b (n + 1) + x_{bb} (n + 1)^2 + g_{bb} l^2, \quad (1)$$

where  $\omega_b$  is the bending harmonic frequency,  $x_{bb}$  and  $g_{bb}$ , are the anharmonic constants, and  $n$  and  $l$  are the quantum numbers for total vibrational excitation and vibrational angular momentum. The anharmonic constants are derived from two sources (1) cubic bend stretch coupling  $\frac{1}{2}\phi_{sbb}q_s(q_{ba}^2 + q_{bb}^2)$  treated in second order, and (2) the direct quartic coupling  $\frac{1}{24}\phi_{bbbb}(q_{ba}^2 + q_{bb}^2)^2$ , where  $q_{ba}$  and  $q_{bb}$  are the two components of the bend in dimensionless normal coordinates and  $q_s$  is the bond stretching mode. Using second order perturbation theory, we get the following expressions for  $x_{bb}$  and  $g_{bb}$ :

$$\begin{aligned} x_{bb} &= \frac{1}{16}\phi_{bbbb} - \frac{1}{16}\phi_{sbb}^2 \left[ \frac{3\omega_s^2 - 8\omega_b^2}{\omega_s(\omega_s^2 - 4\omega_b^2)} \right] \\ &\rightarrow \frac{1}{16}(\phi_{bbbb} - 3\phi_{sbb}^2\omega_s^{-1}), \\ g_{bb} &= -\frac{1}{48}\phi_{bbbb} + \frac{1}{16}\phi_{sbb}^2 \left[ \frac{\omega_s}{\omega_s^2 - 4\omega_b^2} \right] \\ &\rightarrow -\frac{1}{48}(\phi_{bbbb} - 3\phi_{sbb}^2\omega_s^{-1}), \end{aligned} \quad (2)$$

where  $\rightarrow$  refers to the limit that  $\omega_s^2 \gg \omega_b^2$ . In that limit, notice that  $x_{bb} = -3g_{bb}$ . For acetylene,  $\omega_s \sim 3500 \text{ cm}^{-1}$  and  $\omega_b \sim 700 \text{ cm}^{-1}$ , and we get  $\omega_s^2 \sim 25\omega_b^2$  thus showing that this limit is appropriate. The treatment above uses a potential expansion in dimensionless, rectilinear normal modes. McCoy and Sibert recently compared perturbation expansions for linear molecules using both rectilinear and curvilinear coordinates and found that order by order the two approaches give almost identical results.<sup>8</sup>

The harmonic coupling between two equivalent bending modes  $q_1$  and  $q_2$  can be written in terms of  $\lambda(q_{1a}q_{2a} + q_{1b}q_{2b})$ . But we are only interested in near resonant coupling terms that connect states with the same total number of quanta of bending excitation. Thus, we neglect terms which couple states differing by  $2\omega_b$  in energy. In the spirit of Child and Lawton, we introduce an effective HCAO Hamiltonian for the two bending modes of acetylene as

$$\begin{aligned} H &= \omega_b (\hat{n}_1 + \hat{n}_2 + 2) + x_{bb} [(\hat{n}_1 + 1)^2 + (\hat{n}_2 + 1)^2 \\ &\quad - \frac{1}{3}\hat{l}_1^2 - \frac{1}{3}\hat{l}_2^2] \\ &\quad + \lambda(a_{1a}^+ a_{2a} + a_{1b}^+ a_{2b} + a_{2a}^+ a_{1a} + a_{2b}^+ a_{1b}), \end{aligned} \quad (3)$$

where we can write the number operator,  $\hat{n}_i$ , and the vibrational angular momentum operator,  $\hat{l}_i$ , in terms of raising ( $a_{ia}^+$  and  $a_{ib}^+$ ) and lower operators ( $a_{ia}$  and  $a_{ib}$ ) by the relationships

$$\begin{aligned} \hat{n}_i &= a_{ia}^+ a_{ia} + a_{ib}^+ a_{ib}, \\ \hat{l}_i &= i(a_{ia}^+ a_{ib} - a_{ib}^+ a_{ia}). \end{aligned} \quad (4)$$

We now make a transformation from local to normal mode representations by defining

$$\begin{aligned} a_{4a} &= \frac{1}{\sqrt{2}} (a_{1a} + a_{2a}), & a_{5a} &= \frac{1}{\sqrt{2}} (a_{1a} - a_{2a}), \\ a_{4b} &= \frac{1}{\sqrt{2}} (a_{1b} + a_{2b}), & a_{5b} &= \frac{1}{\sqrt{2}} (a_{1b} - a_{2b}), \\ a_{4+} &= \frac{1}{\sqrt{2}} (a_{4a} + ia_{4b}), & a_{4-} &= \frac{1}{\sqrt{2}} (a_{4a} - ia_{4b}), \\ a_{5+} &= \frac{1}{\sqrt{2}} (a_{5a} + ia_{5b}), & a_{5-} &= \frac{1}{\sqrt{2}} (a_{5a} - ia_{5b}). \end{aligned} \quad (5)$$

Substitution of these operators into the Hamiltonian produces a representation in terms of normal mode ladder operators. Because the transformation from bond lengths or angles to dimensionless coordinates has a factor of  $\sqrt{\omega}$ , and the two normal modes have different frequencies, the above ladder operators are not exactly the true normal mode opera-

tors. In the harmonic Hamiltonian the small corrections to obtain the exact normal mode operators [which are on the order of  $(\lambda/\omega)^2$ ] introduce off-resonance couplings that exactly cancel the off-resonance part of the  $k_{12}q_1q_2$  and  $G_{12}p_1p_2$  couplings terms that is neglected in Eq. (3). The resonance part of these couplings make up the coupling term proportional to  $\lambda$ . There is no reason to assume that this exact cancellation will occur for the anharmonic contributions considered in this paper, and thus this approximate transformation must be considered along with the assumption of only harmonic coupling between the anharmonic modes as part of the limitations of the HCAO model.

Using Eqs. (5), we can write the local mode ladder operators and thus also the number and angular momentum operators in terms of the normal mode ladder operators. Substituting these into Eq. (3) gives, after some tedious algebra, the Hamiltonian in the same form as the effective Hamiltonian used by Pliva in his fit to the bending levels of acetylene.<sup>9</sup>

$$\begin{aligned} H &= \omega_4 (\hat{n}_4 + 1) + \omega_5 (\hat{n}_5 + 1) + x_{44} (\hat{n}_4 + 1)^2 + x_{45} (\hat{n}_4 + 1)(\hat{n}_5 + 1) + x_{55} (\hat{n}_5 + 1)^2 \\ &+ g_{44} \hat{l}_4^2 + g_{45} \hat{l}_4 \hat{l}_5 + g_{55} \hat{l}_5^2 + r_{45} (a_{4+}^+ a_{5-}^+ a_{4-} a_{5+} + a_{4-}^+ a_{5+}^+ a_{4+} a_{5-}) \\ &+ s_{45} (a_{4+}^+ a_{4-}^+ a_{5+} a_{5-} + a_{5+}^+ a_{5-}^+ a_{4+} a_{4-}) \\ &+ \frac{1}{2} (r_{45} + 2g_{45}) [(a_{4+}^+)^2 (a_{5+})^2 + (a_{4-}^+)^2 (a_{5-})^2 + (a_{5+}^+)^2 (a_{4+})^2 + (a_{4-}^+)^2 (a_{5-})^2] - \frac{1}{3} x_{bb} \end{aligned} \quad (6)$$

but with the following  $x$ - $K$  relations which express all the normal mode anharmonic and Darling–Dennison-type interaction constants in terms of the single  $x_{bb}$  term,

$$\begin{aligned} \omega_4 &= \omega_b + \lambda, \\ \omega_5 &= \omega_b - \lambda, \\ x_{44} &= x_{55} = \frac{1}{2} x_{bb}, \\ x_{45} &= r_{45} = s_{45} = \frac{4}{3} x_{bb}, \\ g_{44} &= g_{45} = -\frac{1}{6} x_{bb}, \\ g_{45} &= 0. \end{aligned} \quad (7)$$

Table I gives a comparison of the anharmonic constants determined by Pliva with the relationships derived above. It is seen that the relationships fail miserably, not even getting the relative sign of the different terms. This can be contrasted

with  $x$ - $K$  relationships for hydride stretching modes, which are typically found to be accurate to  $\sim 10\%$  or better. What has gone wrong in the present case? Table II shows the anharmonic constants calculated by Strey and Mills,<sup>10</sup> based upon a fit of an anharmonic force field to the spectroscopic constants of acetylene and its isotopomers. The terms contributing to each anharmonic constant are broken down into cubic and quartic terms, respectively. It is seen that a remarkable cancellation of terms occurs in these anharmonic constants. Viewed as separate contributions, the cubic and quartic contributions do obey the  $x$ - $K$  relations to reasonable accuracy. But, the crude model that underlies these relations cannot be expected to reproduce the details of the near cancellations. Thus, in this case, these relations appear to be of no value as a guide in fitting of the spectrum.

An interesting question is why do we have such striking

TABLE I. Comparison of  $x$ - $K$  relations and experimental constants.

Anharmonic constant	Prediction $x$ - $K$ relationship	Observed value ( $\text{cm}^{-1}$ )
$x_{44}$	$\frac{1}{2}x_{bb}$	3.082 (15)
$x_{45}$	$\frac{4}{3}x_{bb}$	-2.406 (14)
$x_{55}$	$\frac{1}{2}x_{bb}$	-2.335 (6)
$g_{44}$	$-\frac{1}{6}x_{bb}$	0.759 (21)
$g_{45}$	0	6.541 (14)
$g_{55}$	$-\frac{1}{6}x_{bb}$	3.490 (8)
$r_{45}$	$\frac{4}{3}x_{bb}$	-6.238 (5)

TABLE II. Contributions to calculated anharmonic terms (in  $\text{cm}^{-1}$ ).

Anharmonic constant	Quartic terms	Cubic terms	Total
$x_{44}$	31.43	-28.30	3.13
$x_{45}$	113.01	-114.63	-1.62
$x_{55}$	33.29	-35.75	-2.46
$g_{44}$	-10.48	10.46	-0.02
$g_{45}$	0	6.54	6.54
$g_{55}$	-11.10	13.99	2.89

cancellation of terms? Consider the following very simple model, where the potential is exactly harmonic in terms of the curvilinear bond stretching and bending coordinates defined by

$$V = \frac{1}{2}k_r \Delta r^2 + \frac{1}{2}k_b \Delta \theta^2,$$

$$\Delta r = \sqrt{x^2 + y^2 + (z + r_e)^2} - r_e,$$

$$\Delta \theta = \tan^{-1} \frac{\sqrt{x^2 + y^2}}{z + r_e}, \quad (8)$$

where  $x, y, z$  are the Cartesian coordinates for the hydrogen atom relative the heavy frame and  $r_e$  is nominally the equilibrium bond length but a true bend–stretch cubic coupling can be removed to first order by defining an effective “pivot” distance which is typically longer than the bond length. In this model, we find that both  $k_s$  and  $k_b$  contribute to  $\phi_{sbb}$  and  $\phi_{bbbb}$  by the following relationships:

$$\phi_{sbb} = \frac{1}{hc} (r_e^2 k_s - 2k_b) \frac{1}{r_e^2} \left( \frac{\hbar^2}{mk_s} \right)^{1/4} \left( \frac{\hbar^2}{mk_b} \right)^{1/2},$$

$$\phi_{bbbb} = \frac{1}{hc} (3r_e^2 k_s - 8k_b) \frac{1}{r_e^2} \left( \frac{\hbar^2}{mk_b} \right). \quad (9)$$

Putting these into Eq. (1) for the value of  $x_{bb}$ , it is found that the cubic and quartic terms give terms

$$x_{bb} = \frac{1}{hc} \frac{1}{16} \left( \frac{\hbar^2}{mr_e^2} \right) \times \beta^{-1} \left( \frac{3 - 8\beta}{1 - 4\beta} \right) [(1 - 4\beta) - (1 - 2\beta)^2]$$

$$x_{bb} \rightarrow \frac{1}{hc} \frac{3}{4} \left( \frac{\hbar^2}{mr_e^2} \right) \beta \quad \text{for } \beta \ll 1, \quad (10)$$

where we have introduced  $\beta = k_b/r_e^2 k_s = (\omega_b/\omega_s)^2 \sim 0.04$  for acetylene. The  $(1 - 4\beta)$  term comes from the quartic contribution and  $(1 - 2\beta)^2$  from the cubic term. The result is  $4\beta^2 \sim 6.4 \times 10^{-3}$  times smaller than either of these terms. For acetylene, this implies a value of  $x_{bb} \sim 0.5 \text{ cm}^{-1}$  which is clearly too small to explain the observed bending anharmonic constants. That the cancellations in Strey and Mills' calculations were not this complete is probably due to the presence of anharmonic terms in the curvilinear force field used in their model. Anharmonic coupling to other vibrational modes is expected to produce contributions to the anharmonic constants as well. For example, the cubic coupling

of the bending modes to the CC stretching mode  $\nu_2$ , i.e.,  $\phi_{244}$  and  $\phi_{255}$ , give contributions to the bending anharmonic constants. Using the Strey and Mills force field these contributions (in  $\text{cm}^{-1}$ ) are calculated to be  $-2.85$  to  $x_{44}$ ,  $-2.33$  to  $x_{45}$ ,  $-1.83$  to  $x_{55}$ ,  $+1.50$  to  $g_{44}$ , and  $+0.82$  to  $g_{55}$ . Notice that while these are only a small part of the total cubic contributions to these constants (see Table II), they are clearly of the same size as the total anharmonic terms, though they do not dominate them either.

It is interesting that the  $g_{45}$  term, which is predicted to be zero in the HCAO model, is the largest of the observed anharmonic constants. In the Strey and Mills force field, it is seen that  $g_{45}$  is the largest anharmonic term only because it does not suffer any cancellation. In this force field, only one anharmonic constant,  $\phi_{345}$  contributes to  $g_{45}$ . In terms of the local mode force field,  $\phi_{345}$  reflects coupling of one CH bond stretch to the bending mode of the other CH bond. Direct quartic anharmonic coupling between the bending modes can make a contribution to the  $g_{45}$  term as well, but the appropriate coupling term was constrained to zero in the Strey and Mills fit.

In summary, we have considered a HCAO model for the bending vibrations in acetylene and have found that it fails to predict, even qualitatively, the observed anharmonic constants. This is attributed to fine cancellation of cubic and quartic contributions. Perhaps, the relations will prove useful in treating the bending vibrations of diacetylene, where one would expect the coupling between the oscillators to be greatly reduced.

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