Quartic anharmonic resonances in acetylenes and haloacetylenes

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Formulas are derived for the quartic anharmonic resonance coefficients observed to be important between C–H stretching and the combination of one quantum of C≡C stretching and two quanta of H–C≡C bending in a number of acetylene molecules. Examples of this resonance are $\nu_1$ with $\nu_1 + \nu_2 + \nu_3$ in $^{12}$C$_2$H$_2$, $\nu_1$ with $\nu_2 + 2\nu_3$ in $^{13}$C$_2$H$_2$, and $\nu_1$ with $\nu_2 + 2\nu_4$ in monofluoroacetylene and monochloroacetylene. The coefficients characterizing the resonances in these examples, which we denote $K_{1,245}$, $K_{1,255}$, and $K_{1,244}$, arise from cubic and quartic terms in the anharmonic force field, in the normal coordinate representation, through second order and first order perturbation treatments respectively, where the second order resonances are calculated by a Van Vleck resonance formalism. The experimentally determined values of these coefficients are compared with values calculated from model anharmonic force fields. © 1995 American Institute of Physics.

I. INTRODUCTION

Accidental anharmonic resonances in vibration–rotation spectra are of interest for two reasons. In the first place they are the key to understanding energy flow within a molecule, because they provide the path between otherwise independent degrees of freedom. In the second place they provide quantitative information on the anharmonic character of the potential energy surface, although it is generally a complex task to relate the resonance coefficients determined from spectral analysis into information on the surface. This paper is concerned with this relationship, for a family of resonances that are characteristically observed in the spectra of acetylene-type molecules.

The resonance between the antisymmetric C–H stretching fundamental $\nu_3$ and the combination band $\nu_2 + \nu_3 + \nu_5$ in acetylene, which leads to an approximately 50/50 mixing of the wave functions, was first analyzed by Lafferty and Thibault1 in 1964, and it has been studied by a number of authors since then both at the fundamental level and through a series of overtones.2–7 There is a similar resonance between the symmetric C–H stretching fundamental $\nu_3$ and the combination band $\nu_3 + 2\nu_5$, which is only a weak resonance in $^{12}$C$_2$H$_2$ where the bands are 48 cm$^{-1}$ apart, but becomes a strong resonance in $^{13}$C$_2$H$_2$ where the corresponding wave functions are again almost 50/50 mixed.8,9 Turning to substituted acetylenes, Borro, Mills, and Mose10 have recently reported a resonance between $\nu_1$ and $\nu_2 + 2\nu_4$ in both monofluoroacetylene HCCF and monochloroacetylene HCCCl, although in both cases the resonance is relatively weak. In all these cases experimental values have been reported for the appropriate anharmonic resonance coefficient, $K_{1,245}$ and $K_{1,255}$ in the case of acetylene, and $K_{1,244}$ for the haloacetylenes.

All these examples involve resonance between C–H stretching and the combination of C≡C stretching plus two quanta of H–C≡C bending, which are always nearly degenerate in molecules containing the H–C≡C moiety. The value of the resonance coefficient is observed to be of the order 10 cm$^{-1}$ in all the above examples. The origin of the resonance is in part a first order coupling due to the corresponding quartic anharmonic force constant, and in part a second order coupling through intermediate states involving two cubic anharmonic force constants and a resonance denominator. There is also a small Coriolis contribution arising from the term $B(j_x^2 + j_y^2)$ in the vibration–rotation Hamiltonian, where $j_x$ and $j_y$ are the vibrational angular momenta perpendicular to the linear molecule axis. The resonances discussed here are analogous to Darling–Dennison resonances,11 which are also effectively a quartic anharmonic resonance effect. In this paper we derive formulas for the effective resonance coefficients and discuss their application.

Formulae for Darling–Dennison resonance coefficients have been presented by Mills and Robiette,12 Pliva,13 Della Valle,14 Lehmann,15 and Law.16 Mills and Robiette12 calculated the Darling–Dennison resonance between hydrogen stretching states, including the coefficient $K_{11,33}$ coupling the overtones $2\nu_1$ and $2\nu_3$ in acetylene, and Pliva13 calculated the coefficient $K_{44,55}$ (which he denotes $s_{45}$) coupling the two bending overtones $2\nu_4$ and $2\nu_5$ in acetylene. Della Valle,14 Lehmann,15 and Law16 have all presented more general formulas for quartic anharmonic resonance coefficients, although none of these authors cover the examples discussed here, $K_{1,245}$, $K_{1,255}$, and $K_{1,244}$, in which one quantum is created and three are annihilated, or vice versa. Only Pliva13 has previously presented a formula for the $K_{3,245}$ resonance coefficient in acetylene; however, we believe his formula to be in error as discussed further below. Finally, we note that a completely general expression that covers all quartic anharmonic resonances has been presented by Aliev and Watson17 in Table V of their review, but it is a nontrivial task to specialize their formulas for particular examples.

We are adopting in this paper a notation for the quartic resonance coefficients which was suggested by Lehmann,15 but which has not been otherwise used before. We use a capital $K$ for the coefficient, with subscripts to represent the vibrational quanta created or annihilated by the off-diagonal operator, and we insert a comma in the subscripts to separate the quanta created from those annihilated (or vice versa). We...
use a capital $K$ for the resonance coefficient to distinguish it from the quartic anharmonic force constant, customarily denoted with a lower case $k$, which makes up one of the contributions to the interaction. (Some authors have previously denoted the resonance coefficient with a lower case $k$, with four subscripts, creating the misleading impression that the only contribution to the resonance is the corresponding term from the quartic anharmonic force field.) We use a comma to separate quanta created from quanta annihilated in order to avoid the ambiguity to which Lehmann drew attention, that in the absence of a separator symbols such as $K_{rstu}$ might suggest a resonance between either $\nu_1 + \nu_2$ and $\nu_3 + \nu_4$, or $\nu_1 + \nu_3$, or $\nu_1 + \nu_4$, or $\nu_2 + \nu_3 + \nu_4$, which would have different theoretical expressions. Thus, for example, the coefficient for the resonance in acetylene which has previously been denoted either $K_{2345}$ or $k_{2345}$ is here denoted $K_{2,3,4,5}$. In all these formulas the second order cubic and first order quartic contributions tend to be similar in magnitude and opposite in sign, leading to some cancellation in the calculation of the final value of the coefficient. The Coriolis contribution is generally significantly smaller than the anharmonic contributions. Similar comments apply to the calculation of the anharmonic constants $x_{ij}$ in the Dunham expansion of the vibrational energy from the perturbation treatment; indeed the $x_{ij}$ are analogous to the quartic resonance coefficients discussed here, except that they are diagonal rather than off-diagonal in the effective Hamiltonian. 

II. PERTURBATION CALCULATION

We represent the Hamiltonian in terms of dimensionless normal coordinates $q_r$, and their conjugate momenta $p_r$. We follow Aliev and Watson in denoting terms involving $m$ powers of vibrational operators ($p$ or $q$) and $n$ powers of rotational operators ($J_1$, $J_2$, or $J_3$) by $H_{mn}$. Thus the cubic and quartic terms in the anharmonic force field are represented by $H_{30}$ and $H_{40}$, respectively. The effective quartic coupling between two nearly accidentally degenerate states $|i\rangle$ and $|j\rangle$ is then given by a contact transformation of the original Hamiltonian, or its matrix elements may be calculated by Van Vleck perturbation theory from the general formula

$$\langle i | H_{40} | j \rangle = \langle i | H_{40} | j \rangle + \sum_k \left\langle i | H_{30} | k \right\rangle \left\langle k | H_{30} | j \right\rangle \frac{E_{ij}^0 - E_{k}^0}{E_{ij}^0}. \tag{1}$$

Here, $E_{ij}^0$ denotes the mean of the unperturbed energies $E_{ij}^0$ and $E_{ij}^0$. The tilde over $H$ on the left-hand side of Eq. (1) is used to indicate a matrix element of the effective (or transformed) Hamiltonian. The first order quartic and the second order cubic contributions in Eq. (1) are expected to be of a comparable magnitude according to the general treatment of orders of magnitude due to Oka. However, if one of the resonance denominators in the sum in the second term is small compared to either of the matrix elements in the numerator, or compared to the difference $E_{ij}^0 - E_{ij}^0$, then that term should be omitted from the sum and the corresponding cubic resonances should be included in a resonance matrix which should be diagonalized numerically.

For acetylene, the indices 1 and 3 label the symmetric and antisymmetric C–H stretching modes, of $\Sigma_g^+$ and $\Sigma_u^+$ symmetry, respectively, the index 2 labels the $\pi\pi^*$ stretching mode of $\Sigma_u^+$ symmetry, and the indices 4 and 5 label the $\Pi_3$ and $\Pi_u$ bending modes. The terms in the Hamiltonian that contribute to the $p_3$ with $p_2 + p_3 + p_5$ resonance are

$$H/\hbar c = k_{2345}q_2^2q_3^2(4q_4 + q_5 - q_4 - q_5)/2 + k_{234q}q_2^2q_3^2q_4^2 + k_{255q}q_2^2q_5^2 + k_{345q}q_2^2q_3q_4q_5/2 + B_j(j_x^2 + j_y^2), \tag{2}$$

where $q_4 = q_{x_4} + iq_{y_2}$ and $q_5 = q_{x_5} - iq_{y_2}$ for the degenerate modes $t=4$ or 5, $q_7 = q_{x_7}^2 + q_{y_2}^2$, and $j_x$ and $j_y$ are the components of the vibrational angular momentum about the molecule fixed $x$ and $y$ axes, given by the expression

$$j_a = \sum_r \sum_s \epsilon_{rs}^a (\omega_s/\omega_1)^{1/2} q_r p_s. \tag{3}$$

We take the $K_{3,2,4,5}$ resonance coefficient to be defined by the following general formula for the $p_3$ with $p_2 + p_3 + p_5$ resonance matrix element:

$$\langle V_1, V_2, V_3, V_4, V_5 | H_{40} | H c | V_1, V_2 + 1, V_3 - 1, V_4 + 1^{\pm 1}, V_5 + 1^{(\pm 1)} \rangle = K_{3,2,4,5} (V_2 + 1) V_3 (V_4 \pm 1) V_5 (V_5 \pm 1) \times (V_5 \pm 2). \tag{4}$$

Applying formula (1) to calculate the coefficient $K_{3,2,4,5}$ we find first order contributions from the quartic force constant $k_{2345}$ and from the Coriolis terms, plus second order cubic contributions to the sum in Eq. (1) from the 12 terms indicated in Table I, which leads to the formula

$$K_{3,2,4,5} = k_{2345} - k_{233k} q_{234}\left[ \frac{1}{\omega_2} + \frac{1}{2 \omega_3 - \omega_2} \right],$$

$$+ k_{244k} q_{234}\left[ \frac{1}{\omega_2} - \frac{1}{2 \omega_3 + \omega_2} \right],$$

$$+ k_{255k} q_{234}\left[ \frac{1}{\omega_2} - \frac{1}{2 \omega_3 + \omega_2} \right],$$

$$+ 4B \epsilon_{2465} q_{234}\left[ \frac{(\omega_3 + \omega_5)(\omega_2 - \omega_1)}{(\omega_2 \omega_3 \omega_4 \omega_5)^{1/2}} \right]. \tag{5}$$

<table>
<thead>
<tr>
<th>Cubic force constants</th>
<th>Energy denominator</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{234}$</td>
<td>$k_{345}$</td>
</tr>
<tr>
<td>$k_{244}$</td>
<td>$k_{345}$</td>
</tr>
<tr>
<td>$k_{255}$</td>
<td>$k_{345}$</td>
</tr>
</tbody>
</table>

Table I. Terms contributing to the perturbation sum in Eq. (1) of the text, for $K_{3,2,4,5}$ in CH$_2$. Terms are labeled by the product of cubic anharmonic force constants and the energy denominators involved. Two terms occur for each energy denominator, one with each sign. There are 12 terms in the sum for $K_{3,2,4,5}$. 

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TABLE II. Terms contributing to the perturbation sum in Eq. (1) of the text, for $K_{1,255}$ in $^{13}$C$_2$H$_2$ (see caption to Table I). There are 12 terms in the sum in this case.

<table>
<thead>
<tr>
<th>Cubic force constants</th>
<th>Energy denominator</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{112}k_{155}$</td>
<td>$\pm(2\omega_1-\omega_2) \approx \pm(\omega_1+2\omega_2)$</td>
</tr>
<tr>
<td>$k_{112}k_{255}$</td>
<td>$\pm\omega_2 \approx \pm(\omega_2-2\omega_1)$</td>
</tr>
<tr>
<td>$k_{122}k_{255}$</td>
<td>$\pm\omega_2 \approx \pm(\omega_2+2\omega_1)$</td>
</tr>
<tr>
<td>$k_{135}k_{255}$</td>
<td>$\pm\omega_2 \approx \pm(\omega_2-2\omega_1)$</td>
</tr>
</tbody>
</table>

The numerical factor $(1/8)$ on the right-hand side of Eq. (4) has been chosen to make the leading term in the expression for $K_{1,245}$ exactly equal to the quartic force constant $k_{2,245}$. Note that the wave functions used in Eq. (4) to define the resonance matrix element have not been Wang transformed to make them eigenfunctions of the parity operator. In practice it may or may not be thought desirable to make this transformation before setting up a resonance matrix; this is a matter of taste. The Wang transformation introduces further numerical factors of $\sqrt{2}$ into the matrix elements. The Coriolis zeta constants appearing in Eq. (5) are to be interpreted as $\xi_{24} = \xi_{2,4a} = -\xi_{2,4b}$, and similarly for $\xi_{35}$.

For the $v_1$ with $v_2 + 2v_3$ resonance in $^{13}$C$_2$H$_2$, of $D_{oh}$ symmetry, the contributing terms in the Hamiltonian are

$$H \sim H_c = k_{1255}g_1q_2g_2^2 + k_{112}g_1^2q_2^2 + k_{124}g_1^2q_4^2 + k_{155}g_4^2q_5^2$$

$$+ k_{255}g_2q_4^2 + B_e(j_x^2 + j_y^2). \quad (6)$$

We take the $K_{1,255}$ Resonance coefficient to be defined by the following formula for the resonance matrix element:

$$\langle v_1, V_2, V_3, V_4' | \hat{H}_{40} | v_1, V_2, V_3, V_4' \rangle = K_{1,255}(1/4)[V_1(5V_2 + 1)\{V_5 + l_2 + 2\}(V_5 - l_2 + 2)]^{1/2} \quad (7)$$

The calculation of $K_{1,255}$ involves second order cubic contributions from the 12 terms indicated in Table II, in addition to the first order contribution from the quartic force constant $k_{1255}$. The expression obtained is

$$K_{1,255} \sim k_{1255} - k_{112}k_{155} \left[ \frac{1}{\omega_2} + \frac{1}{2\omega_1 - \omega_2} \right]$$

$$- k_{122}k_{255} \left[ \frac{1}{\omega_1} + \frac{1}{2\omega_2 - \omega_1} \right]$$

$$- 2k_{155}k_{255} \left[ \frac{1}{\omega_1} - \frac{1}{\omega_2} \right]. \quad (8)$$

In this case there is no Coriolis contribution, because both of the zeta constants that might have contributed, $\xi_{15}$ and $\xi_{25}$, are zero by symmetry.

For the haloacetylene molecules, HCCF and HCCCI, the molecular symmetry is lowered to $C_{2v}$, which allows a number of further contributions to the second order perturbation sum. In the HCCX molecules the indices 1, 2, and 3 label the C–H stretch, C=C stretch, and C–X stretch, all of $\Sigma^+$ symmetry, and 4 and 5 label the H–C=C bond and the C=C–X bond, of $\Pi$ symmetry, respectively. The resonance that has been observed in these molecules is between $v_1$ and $v_2 + 2v_3$ rather than between $v_1$ and $v_2 + 2v_5$. The contributing terms in the Hamiltonian are similar to those in Eq. (6), except that the index 5 has to be changed to 4, and some extra terms have to be added that result from the lower symmetry. The terms required are as follows:

$$H \sim H_c = k_{1244}g_1q_1q_2^2 + k_{112}g_1^2q_2^2 + k_{144}g_1q_2q_3^2 + k_{144}q_1g_4^2q_5^2$$

$$+ k_{244}q_2^2g_3^2 + k_{214}g_2q_3^2q_4^2 + k_{144}q_1q_5^2 + k_{144}q_4^2q_5^2$$

$$+ k_{149}q_1q_5^2 + k_{149}q_4q_5^2 - 2B_e(j_x^2 + j_y^2). \quad (9)$$

We take the $K_{1,244}$ Resonance coefficient to be defined by the following formula for the resonance matrix element:

$$\langle v_1, V_2, V_3, V_4', V_5' \rangle = K_{1,244}(1/4)[V_1(5V_2 + 1)\{V_4 + l_2 + 2\}(V_4 - l_2 + 2)]^{1/2}. \quad (10)$$

In this case there are 20 contributions to the second order perturbation sum to be considered, as indicated in Table III, and there is also a first order Coriolis contribution arising from the nonzero zetas $\xi_{14}$ and $\xi_{24}$, leading to the general formula

$$K_{1,244} \sim k_{1244} - k_{112}k_{144} \left[ \frac{1}{\omega_2} + \frac{1}{2\omega_1 - \omega_2} \right] - k_{122}k_{244}$$

$$\times \left[ \frac{1}{\omega_1} + \frac{1}{2\omega_2 - \omega_1} \right] - (1/2)k_{123}k_{344} \left[ \frac{1}{\omega_1 - \omega_2 + \omega_3} \right]$$

$$+ 2k_{144}k_{244} \left[ \frac{1}{\omega_1} - \frac{1}{\omega_2} \right]$$

$$- k_{145}k_{245} \left[ \frac{1}{\omega_1 - \omega_4 + \omega_5} - \frac{1}{\omega_1 - \omega_4 - \omega_5} \right]$$

$$+ 4B_e\xi_{14}\xi_{24} \left[ \frac{(\omega_1 + \omega_4)(\omega_2 - \omega_4)}{\omega_1\omega_2\omega_4\omega_5} \right]^{1/2}. \quad (11)$$

Again the Coriolis zeta constants in Eq. (11) are to be interpreted as $\xi_{14} = \xi_{1,4a} = -\xi_{1,4b}$, and similarly for $\xi_{24}$. The definition of the resonance coefficients $K$ in Eqs. (7) and (10)
have again been chosen to make the leading term in Eqs. (8) and (11) exactly equal to the corresponding quartic anharmonic force constant.

There are several comments to be made about the formulas listed in Eqs. (5), (8), and (11). The first is that the sign of $K_{3,245}$ depends on what is chosen to be the positive sense of a displacement in $q_1$, $q_2$, $q_4$, and $q_5$; and similarly the signs of $K_{1,245}$ and $K_{1,244}$ depend on the chosen positive sense of $q_1$ and $q_2$. For example $K_{3,245}$ changes sign if the sign of $q_3$ is reversed relative to $q_2$, $q_4$, and $q_5$. Nonetheless, the signs of the calculated values of these resonance constants may not be entirely without meaning, because it may happen that they occur in a resonance matrix with other off-diagonal matrix elements whose signs are known from other information, such as from an \textit{ab initio} calculation. This situation actually occurs for HCCF, as discussed below.

The second comment is that we have written all the expressions for the second order perturbation sums split into partial fractions. For example, Eq. (5) could alternatively be written

$$K_{3,245} = k_{3,245} - k_{3,243}k_{3,145} \left[ \frac{2 \omega_3}{\omega_3(2 \omega_3 - \omega_2)} \right]$$

$$- k_{243}k_{3,45} \left[ \frac{2 \omega_4}{\omega_2(2 \omega_4 + \omega_2)} \right]$$

$$- k_{255}k_{3,45} \left[ \frac{2 \omega_5}{\omega_2(2 \omega_5 + \omega_2)} \right]$$

$$+ 4Bk_{2,43}k_{3,5} \left( \frac{\omega_3 + \omega_5}{\omega_2(\omega_3 + \omega_5)} \right)^{1/2}.$$  \hspace{1cm} (12)

Although this gives a more compact presentation, the advantage of retaining the form in which each denominator is shown separately is that it is easier to modify the expression if one of the denominators becomes so small that the perturbation treatment becomes inappropriate. This happens, for example, in HCCF, where there are significant Fermi resonances between $v_1$ and $v_2 + v_3$, and between $v_2 + v_3$ and $v_2 + 2v_3$, due to the near accidental degeneracy between these three states; in this case it is necessary to set up a resonance matrix including (at least) the states $v_1$, $v_2 + v_3$, and $v_2 + 2v_3$, including the off-diagonal resonance coupling between each of the three pairs. The effective resonance coefficient between $v_2$ and $v_2 + 2v_3$ should then be calculated from Eq. (11) by omitting the contribution with a denominator $(\omega_1 - \omega_2 - \omega_3)$ in the third line of Eq. (11). The coefficient should then be denoted with an asterisk, $K_{1,244}^\ast$, which is the customary warning flag that a term with a resonant denominator has been omitted. In this case the relative signs of the three coefficients $K_{1,244}$, $k_{1,23}$, and $k_{3,45}$ become important in setting up the resonance matrix, because they all appear in off-diagonal matrix elements.

The third comment is that formulas (5), (8), and (11) can in any case be made to appear different by changing the way in which the denominators are written. The assumption of Eq. (1) is that $E_i^0$ and $E_j^0$ are essentially degenerate, so that it makes little difference whether the denominator is written $(E_i^0 - E_k^0)$, or $(E_j^0 - E_k^0)$, or $(E_i^0 - E_j^0) = (E_i^0 + E_j^0 - 2E_k^0)/2$.

The difference between these alternatives should be comparable to corrections due to the third order of perturbation theory, which have in any case been neglected. Thus the term in Eq. (5) which is written

$$-k_{3,245}k_{3,45} \left[ \frac{1}{\omega_2} + \frac{1}{2 \omega_3 - \omega_2} \right]$$

might be written in any of the alternative forms

$$-k_{3,245}k_{3,45} \left[ \frac{1}{\omega_3 - \omega_4 - \omega_5} + \frac{1}{2 \omega_3 - \omega_2} \right]$$

$$-k_{3,245}k_{3,45} \left[ \frac{1}{\omega_2 + \omega_3 + \omega_4 + \omega_5} \right]$$

$$-k_{3,245}k_{3,45} \left[ \frac{1}{\omega_3 - \omega_4 - \omega_5} + \frac{1}{\omega_3 + \omega_4 + \omega_5} \right],$$

where we have made use of the approximate equality $\omega_i = \omega_0 + \omega_q + \omega_r$. We have not actually used the average energy $E_{ij}^0$ in our denominators in Eqs. (5), (8), and (11); we have instead used one of the energies $E_i^0$ or $E_j^0$, choosing the one that makes the expression as simple as possible. If, in fact, it makes a significant difference which of these expressions is used in the energy denominator, then the use of the Van Vleck perturbation formula (1) is probably inappropriate. Similar comments apply to every one of the terms in the second order perturbation sums in Eqs. (5), (8), and (11).

The fourth comment is that these formulas can alternatively be written in terms of the force constants $\phi_{rst}$ rather than the force constants $k_{rst}$, etc., where the $\phi$s are used to define the potential energy as a Taylor series expansion with unrestricted sums over the coordinates and factors of $(1/n!)$, so that $\phi_{rst} = (1/n!) \frac{\partial^2 V}{\partial q_r \partial q_s \partial q_t}$. \cite{Borro, Mills, and Venuti: Quartic anharmonic resonances} Expressions written in terms of $\phi$s are usually simpler for general expressions involving summations, whereas those written in terms of $k$s are more useful for explicit applications where the sums are written out, as in Eqs. (5), (8), and (11). However, the translation is easily made using the relations between the $\phi$s and the $k$s given in the Appendix to the paper by Hoy, Strey, and Mills. \cite{Borro, Mills, and Venuti: Quartic anharmonic resonances} Examples of these relations for cubic constants are $k_{3,235} = (1/2)\phi_{233}$ (for two equal indices), and $k_{3,45} = \phi_{3,45}$ (for three different indices); and for quartic constants $k_{3,245} = \phi_{2345}$ (for four different indices), and $k_{1235} = (1/2)\phi_{1255}$ (where just two of the four subscripts are equal).

Finally, we hope that we have derived these formulas correctly, and that we have included all possible terms in the perturbation sums; it is easy to miss terms. It is for this reason that we have listed all the terms included in our calculations in Tables I, II and III, so that others may check our sums. Each of the three authors of this paper has derived these expressions independently, by different methods (including the use of both the algebraic manipulation programs REDUCE and MATHEMATICA) and we are in agreement. Some years ago Pliva \cite{Pliva} published a formula for $k_{3,245}$, in Eq. (12) of Ref. 13. Pliva’s $\kappa_{3,245}$ is the same as our $k_{3,245}$; Pliva omits the Coriolis contribution. Also his formula differs from ours in the second order terms. However, we have communicated with him since writing this manuscript, and he has been kind enough to tell us that he has located his original derivation
and has determined that there are errors of transcription which account for the differences. Thus our formula for the second order terms in $K_{1,245}$ has been further independently confirmed by Pliva using the contact transformation method.

### III. Applications

Several of the resonance constants discussed here have been determined experimentally from the analysis of high resolution spectra of the molecules concerned, with varying degrees of uncertainty. The value of formulas such as those in Eqs. (4), (7), and (10) is that we should be able to compare values of $K_{1,245}$ calculated from a trial anharmonic force field with the experimental observations. If both the experimental analyses and the model on which the formulas are based are good, then we should be able to use the observed values to refine the anharmonic force field. The relevant terms in the anharmonic force field of the molecules discussed here are only imperfectly known at present, but in Tables IV, V, and VI we present a preliminary comparison of the observed values of these resonance constants with those calculated from anharmonic force fields.

For acetylene we have taken the force field of Strey and Mills, which we have converted to the dimensionless normal coordinate representation to obtain the force constants listed in Table IV. Using these constants in Eqs. (5) and (8) we obtain the values of $K_{3,245}$ and $K_{1,255}$ listed at the bottom of the table. These are compared with the experimentally observed constants in Table VI. The signs of the calculated constants are related to the sense of positive displacements in the normal coordinates; Figure 1 shows positive displacements corresponding to the signs given in the tables. The absolute signs of the observed constants have not been determined, and indeed they could only be determined in a meaningful way in relation to the signs of other resonance constants that might appear in the same resonance matrix, or possibly from the analysis of intensity measurements which...

### Table IV: Selected terms from the anharmonic force field of $^{13}$C$_2$H$_2$ and $^{12}$C$_2$H$_2$ taken from the force field of Strey and Mills, used to evaluate $K_{1,245}$ and $K_{3,245}$. All values are in cm$^{-1}$, except for the Coriolis zeta constants which are dimensionless.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Constant</th>
<th>Value (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C$_2$H$_2$</td>
<td>$K_{1,245}$</td>
<td>$\pm 12.88$ (5)</td>
</tr>
<tr>
<td>$^{12}$C$_2$H$_2$</td>
<td>$K_{1,255}$</td>
<td>(not observed)</td>
</tr>
<tr>
<td>$^{13}$C$_2$H$_2$</td>
<td>$K_{1,245}$</td>
<td>$\pm 12.85$ (50)</td>
</tr>
<tr>
<td>$^{13}$C$_2$H$_2$</td>
<td>$K_{1,255}$</td>
<td>$\pm 6.27$ (5)</td>
</tr>
</tbody>
</table>

### Table V: Selected terms from the anharmonic force field of HCCF and HCCCI, used to evaluate $K_{1,245}$. The cubic terms are taken from the ab initio calculations of Botschewina and co-workers, and the quartic terms are our own estimates (see the text). All values are in cm$^{-1}$, except for the Coriolis zeta constants which are dimensionless.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Constant</th>
<th>Value (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCCF</td>
<td>$K_{1,245}$</td>
<td>$7.5$ (3.0)</td>
</tr>
<tr>
<td>HCCCI</td>
<td>$K_{1,245}$</td>
<td>$5.1$ (3.0)</td>
</tr>
</tbody>
</table>

For HCCF only, these are values of $K_{1,245}$, for which the resonant cubic contribution with denominator $\left(\omega_1 - \omega_0 - \omega_9\right)$ has been omitted from the calculation; see the text.
pointingly different. However, we note from Table IV that least squares to fit all of the currently available spectroscopic information on the force field which deserves attention. We intend to investigate this in future publications.

The observed value of \( K_{3,245} \) for \(^{12}\text{C}_2\text{H}_2\) has been rather precisely determined by several different groups\(^ {1-5}\) who are all in close agreement; the value given in Table VI, \( \pm 18.28 \) \( (5) \) \( \text{cm}^{-1} \), is an average.\(^ {23}\) The calculated value of \(-48.13 \text{ cm}^{-1}\) from the Strey and Mills force field is at first disappointingly different. However, we note from Table IV that \(-48.13 \text{ cm}^{-1}\) is obtained as the difference between large cubic and quartic contributions of opposite sign, plus a small Coriolis contribution. Although the cubic constants in the Strey and Mills force field are probably quite reliable, the quartic force field is not well determined, and curvilinear internal coordinate force constants such as \( f_{\text{Raa}} \) which contribute directly to \( K_{3,245} , \) were simply assumed to be zero (there being no experimental data at that time relating to such constants). Similarly for \(^{13}\text{C}_2\text{H}_2\) the value of \( K_{1,255} \) has been precisely observed.\(^ {6}\) In this case the value is in relatively good agreement with the value calculated from the Strey and Mills force field.

Our tentative conclusion from this comparison for acetylene is that the anharmonic force field could be refined to bring the calculated and observed values of \( K_{3,245} \) and \( K_{1,255} \) into agreement, and that the observed values provide information on the force field which deserves attention. We intend to investigate this in future publications.

For fluoroacetylene we have taken the high quality CCSD(T) \( ab\) \( initio \) calculations of Botschwina and co-workers\(^ {24}\) for the structure and the quadratic and cubic force field, and the \( ab\) \( initio \) quartic force field of Green and co-workers;\(^ {25}\) we have then refined these force constants by least squares to fit all of the currently available spectroscopic constants on HCCF and DCCF, with the exception of the data on \( K_{1,244} \), with strong predication to the \( ab\) \( initio \) quadratic and cubic force field and only weak predication to the \( ab\) \( initio \) quartic force field. We used the ASYM20 program\(^ {26}\) to refine the quadratic force field, and our own anharmonic force field program to refine the cubic and quartic force field. The result is a quadratic–cubic–quartic force field which fits all the data well and is closely similar to both of the \( ab\) \( initio \) calculations.\(^ {24,25}\) The results are shown in Tables V and VI.

Although the agreement is not yet satisfactory, the quartic force field is again not well determined, and we again observe that the calculated value of \( K_{1,244} \) is obtained as a difference between large cubic and quartic contributions of opposite sign, with a small Coriolis contribution. In the case of HCCF we have actually been able to determine the sign of \( K_{1,244} \) in relation to the known sign of \( k_{123} \) and \( k_{344} \), because all three contribute to the resonance matrix involving, for example, the states \( \nu_1 , \nu_2 + \nu_3 \), and \( \nu_2 + 2\nu_4 \).\(^ {9}\) For HCCCl we have used the \( ab\) \( initio \) calculations of Horn et al.\(^ {27}\) (which are not at such a high level as those for HCCF\(^ {25}\)) and we have made an intelligent guess at the quartic force field by analogy with HCCF. The results are also shown in Tables V and VI.

Two other possible sources of the discrepancy between observed and calculated values should be mentioned. The first lies in the fact that in general we must expect constants such as \( K_{r,stt} \) to show some vibrational dependence. The observed values relate to various excited vibrational states, whereas our calculated values relate to equilibrium. However, observations of these constants in various excited vibrational polyads\(^ {6,9,10}\) suggest that the vibrational dependence is less than \( 1 \text{ cm}^{-1} \), so that this seems unlikely to be the cause of any large discrepancy. The second possible complication lies in the neglect of higher order effects of anharmonicity, which have been shown by Lewerenze and Quack.\(^ {28}\) (see also Markuart and Quack,\(^ {29}\) Quack,\(^ {30}\) and Law and Duncan\(^ {31}\)) to lead to significant differences between some Fermi resonance constants determined from effective hamiltonians and the corresponding constants predicted from the anharmonic force fields. However, we have found no indication of these effects for the acetylene related molecules discussed here, and indeed the \( ab\) \( initio \) cubic anharmonic force constants of HCCF\(^ {24,25}\) agree well with the empirically determined Fermi resonance constants for \( k_{123} , k_{233} , \) and \( k_{344} \).

Our general conclusion is that when resonance constants of the type discussed here have been precisely determined from spectral analysis, they provide valuable information on the anharmonic force field. None of the force fields at present available have made any use of this information. We believe that the cause of the discrepancies between the calculated and observed values of \( K_{r,stt} \) in Table VI is not due to either of the effects discussed in the previous paragraph, but lies in the fact that the anharmonic force fields need to be further improved. We are at present working to achieve this.

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23 Note that the authors of Refs. 1–5 have used a variety of definitions of the resonance constant that we denote $K_{3,245}$, defined in our Eq. (4). Consequently, the values quoted for this resonance constant differ by numerical factors, such as $2A^2$; these differences have been discussed and related by Jonas et al. in Ref. 6.