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# Intramolecular vibrational redistribution of energy in the stimulated emission pumping spectrum of acetylene

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Using a combination of low resolution dispersed  $\tilde{A} \rightarrow \tilde{X}$  fluorescence spectra and high resolution stimulated emission pumping, we have spectroscopically identified the first stages of vibrational energy flow in the highly vibrationally excited acetylene prepared by  $\tilde{A} \rightarrow \tilde{X}$  emission over the energy range 5 000–18 000  $\text{cm}^{-1}$ . A detailed study of the stimulated emission pumping (SEP) spectrum of acetylene in the  $E_{\text{VIB}}=7000 \text{ cm}^{-1}$  region, in which we report spectroscopic constants and rovibrational term values for 12 vibrational levels, has conclusively shown that Darling–Dennison resonance between the *cis* and *trans* degenerate bending vibrations is the first step in the redistribution of vibrational energy from the initially excited Franck–Condon bright CC stretch and *trans*-bend vibrational combination levels. This allows an extension of our prior dispersed fluorescence (DF) assignments which suggested the crucial role of Darling–Dennison coupling between the *cis* and *trans* bends in IVR [J. Chem. Phys. **95**, 6336 (1991)]. We prove that the symmetric CH stretch vibration, previously thought to play a crucial role in the redistribution of vibrational energy, is Franck–Condon inactive. We have also shown that vibrational-*l*-resonance among the states with excitation of both degenerate bending modes, when combined with a Fermi resonance which couples CC stretch/*trans*/*cis*-bend excited states to the antisymmetric CH stretch, determines the subsequent flow of vibrational energy after the Darling–Dennison bending resonance. These resonances all scale with vibrational excitation in nearly the simple manner expected for the lowest order anharmonic terms in the Hamiltonian, which allows the prediction of the fastest processes at high energy from a detailed study of the high resolution spectrum at lower energy. We find some interesting rules for vibrational energy flow in the short time dynamics: (i) CC stretch excitation is necessary for stretch–bend coupling; (ii) if  $V_2''$  and  $V_4''$  are the quantum numbers of the initially excited bright state, and  $v_b'' = v_4'' + v_5''$  is the total bending quantum number of a state coupled to that bright state, then  $V_4'' \geq v_b'' \geq (V_4'' - 2V_2'')$ ; (iii) the total stretch quantum number  $n_s'' = (v_1'' + v_2'' + v_3'')$  is also conserved by the short time dynamics. These are severe and well characterized restrictions on the range of quantum numbers accessible to the initial bright state during the first stages of intramolecular vibrational redistribution of energy.

## I. INTRODUCTION

Intramolecular vibrational redistribution of energy (IVR) is the free flow of energy among the vibrational degrees of freedom in a single, isolated molecule. A crucial assumption underlying the widely applicable statistical unimolecular reaction rate theories is that IVR is both complete and rapid on the time scale of a chemical reaction.<sup>1–3</sup> The assumption of rapid IVR suggests that the dynamics of a molecule containing a chemically significant amount of energy is qualitatively different<sup>4</sup> from the normal mode limit familiar from textbooks on molecular spectroscopy.<sup>5</sup> Anharmonic<sup>1,6</sup> and Coriolis<sup>7</sup> resonances have long been believed to cause IVR in highly vibrationally excited mol-

ecules, so that the spectroscopic study of resonances is central to a qualitative picture and quantitative understanding of vibrational energy flow in the same way that the study of infrared and Raman spectra can determine molecular structure. Efforts to unravel the various factors necessary for an understanding of IVR at low vibrational energy,<sup>8</sup> in overtone spectra,<sup>6,9–11</sup> and electronic absorption spectra<sup>12</sup> are being made by a number of groups. The work presented here is part of an effort to understand the fastest IVR steps as a function of vibrational energy in acetylene. The anharmonic resonances discussed here for acetylene seem to obey the simple scaling with vibrational quantum numbers predicted by the lowest order anharmonic coupling terms in the Hamiltonian. This means that detailed studies at modest energies can yield tremendous insights into the short-time dynamics at high energy by simple scaling, and that a breakdown of simple scaling indicates new aspects of the dynamics.

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In infrared and Raman spectra, the effects of resonances on the spectrum are *usually* subtle shifts (perturbations) of the vibrational energies and rotational constants (a measure of the vibrationally averaged structure) which can only be detected by a careful deperturbation. Occasionally, due to an “accidental” degeneracy, the perturbing states will appear in the spectrum as extra, unexpected bands. A classic example, first explained by Fermi<sup>13</sup> and treated comprehensively by Dennison<sup>14</sup> is the appearance of two Raman bands near the one Raman active fundamental  $\nu_1$  of CO<sub>2</sub>. The off-diagonal matrix elements due to anharmonic resonance, in which the vibrational quantum numbers  $\nu_i$  change by  $n_i$  units, scale roughly as  $\Pi \nu_i^{(n_i/2)}$  and thus increase dramatically and predictably with increasing vibrational excitation. The number of levels in each polyad, or group of levels capable of interacting via a given resonance, also increases rapidly with vibrational excitation, since a given change in quantum numbers can be sequentially repeated.<sup>6,8,14–16</sup> However, vibrational resonances are far more prevalent than suggested by the well known “accidental resonances” and nonresonant anharmonic couplings, which are detectable only by deperturbation of very precise data on the low energy vibrational levels observed in infrared and Raman spectra can have profound and predictable effects on the vibrational structure and dynamics at higher energy.<sup>12</sup>

Resonances break down both the physical significance of vibrational and rotational projection quantum numbers as a description of the wave functions and the practical utility of quantum numbers as labels which are simply related to the energy and spectroscopic selection rules. If resonances are strong, so that correlation of the states in the zero-order model to the actual molecular wavefunctions is ambiguous, it may still be possible to assign and deperturb groups of states interacting by well understood resonances. Although the spectroscopic constants obtained from such a deperturbation contain a great deal of information about the potential surface, the primary goal of this paper is to establish the energy flow pathway.

Anharmonic resonances identified by detailed spectroscopic deperturbations of high resolution infrared and Raman spectra play an important role, but because the detection of a resonance requires deviations from simple energy level formulas (derived from Van Vleck perturbation theory) which exceed the spectroscopic resolution, resonances across large energy gaps may not be detected in infrared and Raman spectra. For example, the Darling–Dennison resonance between the two acetylene bending vibrations discussed here has not led to detectable perturbations of the energy level pattern in the low lying levels. The effects of the off-diagonal matrix elements amount to shifts of about 2 cm<sup>-1</sup> for the highest bending levels in the ir spectra, but because the shifts increase only gradually with the number of vibrational quanta, the levels can be quantitatively fit without off-diagonal matrix elements. The shifts due to the off-diagonal matrix elements are simply absorbed into the effective diagonal spectroscopic constants (e.g.,  $\chi_{ij}$ 's). The leverage gained by increasing the number of vibrational quanta may cause a resonance, which led to

only smooth changes along a vibrational progression at low vibrational excitation, to reveal itself as a mutual repulsion and mixing of the resonating states with increasing vibrational quantum numbers, as the Darling–Dennison bend resonance does here.

Since dynamics is simple for short time intervals, which correspond to large energy intervals, it should be possible to understand sufficiently low resolution spectra, provided that these spectra are free of inhomogeneous broadening (i.e., the spectra originate from a single eigenstate).<sup>17</sup> In a study of the low resolution (30 cm<sup>-1</sup>) acetylene  $\tilde{A} \rightarrow \tilde{X}$  dispersed fluorescence (DF) spectrum which originated from single rovibronic levels of the  $\tilde{A}$  state, we showed that *identical* features, and at higher energy, identical groups of features, appeared in DF spectra recorded from two different vibrational levels of the  $\tilde{A}$  state as shown in Fig. 7 of our prior paper.<sup>15</sup> By identical features, we mean unresolved groups of lines with the same intensity envelope that appear at the same  $\tilde{X}$ -state vibrational energy: i.e., the features obey the Ritz combination principle. A comparison between the DF spectra and higher (0.5 cm<sup>-1</sup>) resolution stimulated emission pumping (SEP) spectra revealed that the low resolution features are not transitions to single eigenstates, but are composed of transitions to several vibrational levels.

If the eigenstates observed in SEP were independent zero-order bright states, there would be no reason to expect independently bright vibrational states to have exactly the same relative intensities in spectra originating from two different  $\tilde{A}$ -state vibrational levels. The DF spectra would not even be expected to have intensity maxima in the same place. However, the ground state dynamics for a zero-order Franck–Condon bright state must be the same, regardless of which  $\tilde{A}$ -state vibrational level it is prepared from, thus guaranteeing the same relative intensity patterns under an isolated feature. Since the same low resolution features are observed in two different DF spectra, the low resolution features are the zero-order bright states (in the case of identical groups of features, each group represents a zero-order bright state). The eigenstates observed under a feature in the SEP spectra all steal their intensity by mixing with the single zero-order Franck–Condon bright basis state which gives the feature its intensity. The appearance of identical groups of DF features suggests that all of the features within a group gain their intensity from a single bright state.

In Ref. 15, we showed that most of the DF features could be assigned CC stretch and *trans*-bend quantum numbers. The vibrational energies of the features could be represented by extrapolation from a slightly refined anharmonic expansion which represents the energies of the single vibrational levels observed in infrared and Raman spectroscopy. Furthermore, the relative intensities of the features were in accord with the Franck–Condon principle. However, there was some ambiguity about the assignment of the DF progressions which contained the states tentatively assigned to the CH stretch by Abramson *et al.*,<sup>18</sup> and it was suggested that *cis*-bend levels, appearing through a previously undetected anharmonic resonance, might better

explain some features of the DF and SEP spectra.

In this paper, we provide the details of a high resolution study which has identified a series of strong anharmonic resonances responsible for the systematic redistribution, on a timescale of a few hundred femtoseconds, of the vibrational energy deposited in acetylene by  $\tilde{A} \rightarrow \tilde{X}$  emission. The most essential features of this analysis have already been reported in a brief communication.<sup>19</sup> In particular, we prove here that a previously undetected Darling–Dennison resonance between the *cis* and *trans*-bending vibrations is the first step in the IVR path for acetylene vibrational levels prepared by stimulated emission pumping in the  $E_{\text{VIB}} = 7000 \text{ cm}^{-1}$  region. This analysis leads to definite assignments for all of the 50 features below  $14\,000 \text{ cm}^{-1}$  in the dispersed fluorescence spectrum in terms of CC stretch/*trans*-bend excited Franck–Condon bright states and their *cis*-bend Darling–Dennison resonance companions. Using the results of our prior study of the dispersed fluorescence spectrum of acetylene,<sup>15</sup> we infer that *the IVR pathway identified here is the first step in the flow of vibrational energy from the initially excited CC stretch and trans-bend combination vibrations into the remaining vibrational modes up to  $18\,000 \text{ cm}^{-1}$  vibrational energy.* The DD resonance in particular becomes more prominent with increasing excitation of the *trans*-bend due to a catastrophic degeneracy of the entire  $v_b'' = (v_4'' + v_5'')$  manifold near  $v_b'' = 16$ , which causes a massive perturbation of all DF features with  $v_4'' = 14$ . States with CH stretching excitation, previously thought to play an important role in the redistribution of vibrational energy,<sup>20</sup> are apparently absent in  $\tilde{A} \rightarrow \tilde{X}$  emission owing to small Franck–Condon factors for all  $v_1' = 0 \rightarrow v_1'' \neq 0$  transitions.

## II. BACKGROUND

The  $\tilde{A} \rightarrow \tilde{X}$  transition moment of acetylene is perpendicular to the plane of the *trans*-bent  $\tilde{A}$  state. This orientation of the transition moment implies  $\Delta K \equiv K' - l'' = \pm 1$  rotational selection rules.<sup>21</sup> Because of the large change in equilibrium *trans*-bending angle and carbon–carbon (CC) bond length between the triply CC bonded, linear  $\tilde{X}$  state and the doubly CC bonded, *trans*-bent  $\tilde{A}$  state, the  $\tilde{A} \rightarrow \tilde{X}$  emission spectra contain long progressions in combinations of the “CC” stretch,  $v_2''$ , and the *trans*-bend,  $v_4''$ , as expected from the Franck–Condon principle. Since there is a slight decrease in CH bond length on  $\tilde{A} \rightarrow \tilde{X}$  emission but no distortion or frequency change for the antisymmetric CH stretch,  $v_3''$ , and the *cis*-bend,  $v_5''$ , Abramson *et al.*<sup>18</sup> tentatively assigned two additional progressions as built on symmetric “CH” stretch,  $v_1''$ , excitation.

Recently, we suggested that the two additional progressions observed in low resolution dispersed fluorescence spectra of the acetylene  $\tilde{A} \rightarrow \tilde{X}$  transition might be better explained by a previously undetected strong  $\Delta v_4 = -\Delta v_5 = \pm 2$  Darling–Dennison (DD) resonance transferring intensity from the Franck–Condon bright *trans*-bend,  $v_4''$ , to the Franck–Condon dark *cis*-bend,  $v_5''$ .<sup>15</sup> This reassignment of entire progressions is possible because  $v_1'$  is accidentally almost equal to  $v_2'' + 2v_5''$ . The observed intensity

patterns posed some difficulties for the reassignment to *cis*-bend excited levels in Ref. 15, so that this reassignment was somewhat tentative, and we proposed a test based on the vibrational-*l*-doubling effect in vibrational states with excitation of both degenerate bending vibrations.

If both degenerate vibrations ( $v_4''$  and  $v_5''$ ) are excited, the individual vibrational angular momenta,  $l_4''$  and  $l_5''$ , couple to produce the total vibrational angular momentum,  $l'' = l_4'' + l_5''$ , and more than one combination of  $l_4''$  and  $l_5''$  may be associated with each value of  $l''$  for given  $v_4''$  and  $v_5''$ .  $\Delta l_4 = -\Delta l_5 = \pm 2$  (i.e.,  $\Delta l'' = 0$ ) vibrational-*l*-resonance between states which differ only in the separate vibrational angular momentum quantum numbers  $l_4''$  and  $l_5''$  will destroy the separate  $l_4''$  and  $l_5''$  quantum numbers and spread the intensity associated with a given  $l_4''$ ,  $l_5''$ ,  $l''$  bright state among levels with the same symmetry and remaining quantum numbers.<sup>22</sup> “Extra”  $l'' = 2$  levels (i.e., without  $l'' = 0$  partners in the spectrum) can appear through the combined effect of vibrational-*l*-resonance and Darling–Dennison bend resonance. We report here definitive confirmation of the Darling–Dennison bend resonance hypothesis by detection and fitting of these extra  $l'' = 2$  levels in the SEP spectrum.

## III. NOTATION, PHASE CONVENTION, AND MATRIX ELEMENTS

The vibrational levels of the linear ground electronic state of acetylene are labeled  $(v_1, v_2, v_3, v_4, v_5)^l$  where  $v_1'$  is the symmetric CH stretch ( $\sigma_g^+$  symmetry),  $v_2'$  is the CC stretch ( $\sigma_g^+$ ),  $v_3'$  is the antisymmetric CH stretch ( $\sigma_u^+$ ),  $v_4'$  is the *trans*-bend ( $\pi_g$ ) with vibrational angular momentum  $l_4''$ ,  $v_5'$  is the *cis*-bend ( $\pi_u$ ) with vibrational angular momentum  $l_5''$ , and  $l'' = l_4'' + l_5''$  is the total vibrational angular momentum. For levels with  $l_4'' = -l_5'' \neq 0$ , an additional subscript  $( )_{\pm}^0$  denotes the parity of the  $J'' = 0$  level. (Levels with  $l_4'' = -l_5'' \neq 0$  always come in pairs of opposite parity.) Vibrational levels of the *trans*-bent  $\tilde{A}$  state will be labeled  $(v_1', v_2', v_3', v_4', v_5', v_6')$  where  $v_1'$  is the symmetric CH stretch ( $a_g$ ),  $v_2'$  is the CC stretch ( $a_g$ ),  $v_3'$  is the *trans* bend ( $a_g$ ),  $v_4'$  is the torsion ( $a_u$ ),  $v_5'$  is the antisymmetric CH stretch ( $b_u$ ), and  $v_6'$  is the antisymmetric in-plane bend ( $b_u$ ). The  $\tilde{A}$  state is a near prolate asymmetric top, and rotational levels are labeled  $J_{K_a, K_c}$  where  $K_a$  is the projection of the angular momentum onto the *a*-inertial axis (axis of least moment of inertia, roughly along the CC bond) and  $K_c$  is (formally) the projection of the angular momentum onto the *c*-inertial axis (axis of greatest moment of inertia which is perpendicular to the molecular plane and through the center of mass). Note that due to the change in symmetry, the *trans* bend is labeled  $v_4''$  in the  $\tilde{X}$  state and  $v_3''$  in the  $\tilde{A}$  state,  $v_3''$  correlates to  $v_5''$ , the degenerate vibration  $v_5''$  correlates to both  $v_4''$  and  $v_6''$  (which become degenerate at the linear geometry), and  $l''$  correlates to  $K' = K_a$ .

Following the accepted spectroscopic convention,<sup>23</sup> rovibronic levels with total parity  $(-1)^J$  or  $-(-1)^J$  will be denoted *e* or *f*, respectively. The electric dipole selection rule  $+\leftrightarrow-$  implies  $e \leftrightarrow f$  for  $Q$  ( $\Delta J = 0$ ) transitions

and  $e \leftrightarrow e$ ,  $f \leftrightarrow f$  for  $R$  or  $P$  ( $\Delta J = \pm 1$ ) transitions. According to spectroscopic convention, SEP transitions will be labeled  $P$  or  $R$  according to whether  $J''$  (the total angular momentum of the lower  $\bar{X}$  level) is greater or less than  $J'$  (the total angular momentum of the upper  $\bar{A}$  level).

An extended molecular symmetry group<sup>24–27</sup> is used to classify the symmetry of separate rotational and vibrational states of the linear molecule in the same manner as for a symmetric top. Of course, the only states of the fictitious symmetric top which occur for a linear molecule are those where the projection of the total angular momentum along the linear axis equals the total vibrational angular momentum. Symmetric top rotational basis states will be denoted  $|J, k\rangle$  where  $J$  is the total angular momentum and  $k$  is the (signed) projection of  $J$  with absolute value  $K'$  or  $l''$ . The transformation of a symmetric top wave function under  $\sigma_v$ , the reflection in the molecule fixed plane which determines the parity (+/– label), is taken as

$$\sigma_v |J, k\rangle = (-1)^{J-k} |J, -k\rangle. \quad (1)$$

For  $k \neq 0$ , the above signed- $k$  basis states do not have a definite parity, so that parity-basis states must be formed from linear combinations  $1/\sqrt{2}(|J, k\rangle \pm |J, -k\rangle)$  of signed- $k$  basis states. Rotational basis states with a definite parity will be denoted  $|J, K', e$  or  $f\rangle$  in the  $\bar{A}$  state or  $|J'', l'', e$  or  $f\rangle$  in the  $\bar{X}$  state. The transformation of the  $\bar{X}$  state vibrational wave functions under  $\sigma_v$  is taken as

$$\sigma_v |v_1, v_2, v_3, v_4^l, v_5^l\rangle = |v_1, v_2, v_3, v_4^{-l}, v_5^{-l}\rangle. \quad (2)$$

Thus, it is also necessary to form linear combinations of vibrational states with  $l'' = -l'' \neq 0$ : the symmetric linear combinations have  $\Sigma^+$  vibrational symmetry and the anti-symmetric linear combinations have  $\Sigma^-$  vibrational symmetry, corresponding to the subscripts used above. The above notation and phase conventions are in agreement with most recent work on acetylene,<sup>21</sup> but it should be noted that the phase convention chosen here differs from that used by Pliva.<sup>28</sup>

#### IV. ANHARMONIC RESONANCES

The Dunham expression for the vibration–rotation energy of a linear polyatomic molecule above the zero-point level [Ref. 5, Eq. (II.284)] is  $T_{vr} = G_v + F_r$ , where

$$G_v = \sum_i \omega_i^0 v_i + \sum_{i < j} x_{ij}^0 v_i v_j + \sum_{i < k < l} g_{ijkl}^0 v_i v_j v_k v_l + \dots - B_v J^2 \quad (3)$$

and

$$F_r = B_v J(J+1) - D_v [J(J+1) - l^2]^2 + \dots \quad (4)$$

with

$$B_v = B_0 - \sum_i \alpha_i v_i + \sum_{i < j} \gamma_{ij} v_i v_j + \sum_{i < k < l} \gamma^{ijkl} v_i v_j v_k v_l + \dots \quad (5)$$

The indices  $i$  and  $j$  range over all five normal modes but  $t$  and  $t'$  are restricted to the doubly degenerate bending vibrations. Note that the term  $B_v J^2$  has been absorbed into the vibrational energy so that, if the rotational energy is given by Eq. (4), a plot of rotational term values  $T_{vr}$  as a

TABLE I. Spectroscopic constants (in  $\text{cm}^{-1}$ ) for acetylene.<sup>a</sup>

$\omega_1^0$	3398.74 <sup>b</sup>	$x_{22}^0$	–7.39 <sup>c</sup>	$x_{55}^0$	–2.335 <sup>d</sup>
$\omega_2^0$	1981.71 <sup>c</sup>	$x_{23}^0$	–6.10 <sup>c</sup>		
$\omega_3^0$	3316.09 <sup>b</sup>	$x_{24}^0$	–12.48 <sup>f</sup>	$g_{44}^0$	0.759 <sup>d</sup>
$\omega_4^0$	609.016 <sup>d</sup>	$x_{25}^0$	–1.57 <sup>f</sup>	$g_{45}^0$	6.541 <sup>d</sup>
$\omega_5^0$	729.170 <sup>d</sup>			$g_{55}^0$	3.490 <sup>d</sup>
		$x_{33}^0$	–27.41 <sup>b</sup>		
$x_{11}^0$	–25.87 <sup>b</sup>	$x_{34}^0$	–6.96 <sup>c</sup>	$r_{45}^0$	–6.238 <sup>d</sup>
$x_{12}^0$	–12.62 <sup>a</sup>	$x_{35}^0$	–8.69 <sup>c</sup>		
$x_{13}^0$	–105.09 <sup>c</sup>			$ K_{1133}^0 $	105.83 <sup>b</sup>
$x_{14}^0$	–15.58 <sup>c</sup>	$x_{44}^0$	3.082 <sup>d</sup>	$ K_{1234}^0 $	16.43 <sup>h</sup>
$x_{15}^0$	–10.85 <sup>f</sup>	$x_{45}^0$	–2.406 <sup>d</sup>	$ K_{2345}^0 $	18.28 <sup>i</sup>

<sup>a</sup>Except for  $x_{12}^0$ , derived from  $(\nu_1 + \nu_2 + \nu_3)$  in Ref. 16, all  $x_{ij}^0$  constants are derived from the combination level  $(\nu_i + \nu_j)[2\nu_i]$  and the fundamentals.

<sup>b</sup>Of the constants  $\omega_1^0$ ,  $\omega_3^0$ ,  $x_{11}^0$ ,  $x_{33}^0$ , and  $K_{1133}^0$ , only  $\nu_1 = \omega_1^0 + x_{11}^0 = 3372.87 \text{ cm}^{-1}$  (Ref. 39), the deperturbed value  $\nu_3^0 = \omega_3^0 + x_{33}^0 = 3288.68 \text{ cm}^{-1}$  (Ref. 35), and the sum  $(x_{11}^0 + x_{33}^0) = -53.28 \text{ cm}^{-1}$  derived from the average of  $2\nu_1 = 6709.01 \text{ cm}^{-1}$  (Ref. 16) and  $2\nu_3^* = 6507.52 \text{ cm}^{-1}$  (see h) are experimentally known.  $x_{13}^0 \approx 2(x_{11}^0 + x_{33}^0)$  suggests that local mode  $x$ - $K$  relations (Refs. 16, 45) for the dominant contributions to  $x_{11}^0$ ,  $x_{33}^0$ ,  $x_{13}^0$ , and  $K_{1133}^0$  can be used to estimate  $K_{1133}^0$  as the average of  $x_{13}^0$  and  $2(x_{11}^0 + x_{33}^0)$ . Deperturbation based on this estimate yields  $2\nu_1^0 = 6694.00 \text{ cm}^{-1}$  and  $2\nu_3^0 = 6522.54 \text{ cm}^{-1}$ .

<sup>c</sup>Reference 39.

<sup>d</sup>Reference 22.

<sup>e</sup>From  $(\nu_1 + \nu_3) = 6556.46 \text{ cm}^{-1}$  (Ref. 16).

<sup>f</sup>Reference 16.

<sup>g</sup> $K_{1133}^0$  and  $K_{1234}^0$  are defined in Ref. 16 and  $K_{2345}^0$  is defined in Eq. (9).

<sup>h</sup>Deperturbed from the observed (Ref. 16) energies  $2\nu_3 = 6502.32 \text{ cm}^{-1}$ ,  $(\nu_1 + \nu_2 + 2\nu_4^0) = 6514.01 \text{ cm}^{-1}$ , and  $G_{(1,1,0,2,0)} = 6508.81 \text{ cm}^{-1}$  calculated from Eq. (3). The “partially deperturbed” (for  $K_{1234}^0$ ) energy of  $2\nu_3$  is denoted  $2\nu_3^*$ .

<sup>i</sup>Calculated from the off-diagonal matrix element in Ref. 35 (see the text).

function of  $J(J+1)$  has  $y$ -intercept  $G_v$ . This definition differs from most prior work, but we find it less confusing. Since  $(g_{44} - B_v) < 0$ , the *trans*-bend rovibrational levels  $(0,0,0,2^0,0)^0$  lie energetically below those of  $(0,0,0,2^0,0)^0$ , and the inclusion of the  $B_v J^2$  term in the vibrational energy ensures that the vibrational energies reflect the measured energetic ordering of the rovibrational levels.<sup>29</sup> With this definition  $G_{(0,0,0,1^0,0)^1} = 611.693 \text{ cm}^{-1}$ . We have determined a set of  $\omega_i^0$  and  $x_{ij}$  constants from what we believe to be the best available data when perturbations are taken into account. This set of constants is presented in Table I. The  $\alpha_i$  in Eq. (5) are taken from Strey and Mills.<sup>30</sup>

Actually, the Dunham expansion provides a poor representation of the observed vibration–rotation energies of acetylene due to a number of resonances which cannot be adequately treated by perturbation theory (i.e., the traditional contact transformation approach). This difficulty is analogous to the resonance denominators which Poincaré showed prevent the convergence of classical perturbation theory everywhere in phase space.<sup>31</sup> Only the simplest terms in the potential energy, which give rise to the resonances observed here, will be reviewed.

In symmetry coordinates, there are two types of quartic coupling between the doubly degenerate *trans* and *cis* bending vibrations. (Direct cubic coupling between the  $\pi$  symmetry bending modes is not allowed by symmetry.) The physical interpretation of this is that when acetylene is bent during the course of one bending vibration, the po-

tential energy for the second bending vibration depends on *both* the amplitude *and* the direction of the second bending vibration relative to the first bending vibration. In dimensionless normal coordinates, the quartic coupling terms in the bending potential are  $k_{4455}\rho_4^2\rho_5^2$  and  $k_{4545}\rho_4^2\rho_5^2\cos^2(\tau)$ , where  $\rho_4$  and  $\rho_5$  are the amplitudes for *trans* and *cis* bending, respectively, in cylindrical coordinates and  $\tau$  is the dihedral angle between the two bending vibrations. If  $\chi_t$  is the bending phase angle for degenerate mode  $t$  measured from the  $\sigma_v$  plane which determines the parity, then  $\tau = \chi_4 - \chi_5$ . Using the matrix elements for the two-dimensional harmonic oscillator (Ref. 27, p. 287) each power of  $\rho e^{i\chi_t}$  raises or lowers  $v_t$  by one and raises  $l_t$  by one, while  $\rho e^{-i\chi_t}$  raises or lowers  $v_t$  by one and lowers  $l_t$  by one. Note that since the potential depends only on the relative angle between the two bending groups, vibrational resonances do not couple states with different total  $l$ .<sup>32</sup> Thus, two terms in the quartic potential contribute to the diagonal constant  $x_{45}$  in Eq. (3) for the vibrational energy ( $\Delta v_4 = \Delta v_5 = \Delta l_4 = \Delta l_5 = 0$ ), as well as to off-diagonal matrix elements for Darling–Dennison resonance (two types:  $\Delta v_4 = -\Delta v_5 = \pm 2$ ,  $\Delta l_4 = \Delta l_5 = 0$  and  $\Delta v_4 = -\Delta v_5 = \pm 2$ ,  $\Delta l_4 = -\Delta l_5 = \pm 2$ ), and off-diagonal matrix elements for vibrational- $l$ -resonance and doubling ( $\Delta v_4 = \Delta v_5 = 0$ ,  $\Delta l_4 = -\Delta l_5 = \pm 2$ ). It turns out (see the Appendix) that if the potential is approximated by the most general quadratic+cubic+quartic force field, the off-diagonal Darling–Dennison spectroscopic constant,  $s_{45}$ , [Eq. (6) below] can be estimated from known spectroscopic constants.<sup>22</sup>

In the signed- $l$ -basis, the off-diagonal matrix elements for DD resonance are

$$\langle v_1, v_2, v_3, v_4^l, v_5^l | \mathcal{H} | v_1, v_2, v_3, (v_4 - 2)^l, (v_5 + 2)^l \rangle = (1/4)s_{45} \sqrt{(v_4 - l_4)^2 - l_5^2} \quad (6)$$

$$\langle v_1, v_2, v_3, v_4^l, v_5^l | \mathcal{H} | v_1, v_2, v_3, (v_4 - 2)^{l_4 \mp 2}, (v_5 + 2)^{l_5 \pm 2} \rangle = (1/16)(r_{45} + 2g_{45}) \times \sqrt{(v_4 \pm l_4 - 2)(v_4 \pm l_4)(v_5 \pm l_5 + 2)(v_5 \pm l_5 + 4)}. \quad (7)$$

In the signed- $l$ -basis, the matrix elements for vibrational- $l$ -resonance and doubling are

$$\langle v_1, v_2, v_3, v_4^l, v_5^l | \mathcal{H} | v_1, v_2, v_3, v_4^{l_4 \mp 2}, v_5^{l_5 \pm 2} \rangle = (1/4)r_{45} \sqrt{(v_4 \pm l_4)(v_4 \mp l_4 + 2)(v_5 \mp l_5)(v_5 \pm l_5 + 2)}. \quad (8)$$

Vibrational- $l$ -resonance and doubling in the lower bending combination bands [ $v_b'' = (v_4'' + v_5'') \leq 4$ ] of acetylene have been systematically studied by Pliva,<sup>22</sup> and more recently by Herman and co-workers.<sup>33</sup>

The 2345 Fermi resonance, due to potential terms such as  $k_{2345}q_2q_3\rho_4\rho_5\cos(\tau)$ , yields nonzero matrix elements

$$\langle v_1, v_2, v_3, v_4^l, v_5^l | \times \mathcal{H} | v_1, (v_2 + 1), (v_3 - 1), (v_4 + 1)^{l_4 \pm 1}, (v_5 + 1)^{l_5 \mp 1} \rangle = -(1/8)K_{2345} \sqrt{(v_2 + 1)v_3(v_4 \pm l_4 + 2)(v_5 \mp l_5 + 2)}. \quad (9)$$

Note that the spectroscopic constant  $K_{2345}$  contains contributions from other potential constants besides  $k_{2345}$  (Ref. 22).  $(v_2 + v_4 + v_5 - 1)_+$  is almost exactly degenerate with the  $v_3$  fundamental of acetylene, and appears in the infrared spectrum with intensity roughly equal to that of the  $v_3$  fundamental through Fermi resonance, Eq. (9).<sup>34–38</sup> The 2345 Fermi resonance has been extensively studied because of its importance for combination bands of  $v_3''$  with  $v_2''$ ,  $v_4''$ , and  $v_5''$ .<sup>39,40</sup> However, this resonance is overshadowed by other resonances for the infrared active overtones of  $v_3''$ .<sup>16,41</sup> For the  $J=0$  level of the fundamental, the matrix elements in the signed- $l$ -basis are

$$\mathcal{H} = \begin{bmatrix} G_{(0,0,1,0,0)} & -K_{2345}/4 & -K_{2345}/4 \\ -K_{2345}/4 & G_{(0,1,0,1+1,1-1)0} & r_{45} \\ -K_{2345}/4 & r_{45} & G_{(0,1,0,1-1,1+1)0} \end{bmatrix}. \quad (10)$$

Time reversal symmetry requires that  $G_{(0,1,0,1-1,1+1)0} = G_{(0,1,0,1+1,1-1)0}$ , as given by Eq. (3). Time reversal simplifies the form of the matrix elements in a basis where  $l$  is a signed quantum number, but the matrix  $\mathcal{H}$  can be block diagonalized by transforming to basis states  $(1/\sqrt{2}) \times (|v_1, v_2, v_3, v_4^l, v_5^l\rangle \pm |v_1, v_2, v_3, v_4^{-l_4}, v_5^{-l_5}\rangle)$ , which have a definite parity. Let

$$\mathcal{O} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \end{bmatrix}. \quad (11)$$

The orthogonal transformation  $\mathcal{H}' = \mathcal{O}^T \mathcal{H} \mathcal{O}$  block diagonalizes the matrix into  $\Sigma_u^+$  and  $\Sigma_u^-$  blocks. Although there is a coupling between the signed- $l$ -basis states, there is no coupling between the  $\Sigma_u^+$  and  $\Sigma_u^-$  blocks. A  $\Sigma^-$  state can never borrow intensity from a  $\Sigma^+$  state because  $\Sigma^+ \sim \Sigma^-$  coupling is forbidden by symmetry.<sup>42</sup> The block diagonalized matrix,  $\mathcal{H}'$ , is

$$\mathcal{H}' = \begin{bmatrix} G_{(0,0,1,0,0)} & -\sqrt{2}K_{2345}/4 & 0 \\ -\sqrt{2}K_{2345}/4 & (G_{(0,1,0,1+1,1-1)0} + r_{45}) & 0 \\ 0 & 0 & (G_{(0,1,0,1+1,1-1)0} - r_{45}) \end{bmatrix}. \quad (12)$$

It is important to note that the factor of  $\sqrt{2}$  arising from the transformation from the signed- $l$ -basis to the parity basis has been neglected in Refs. 16, 34, 35, 37, 38, and 41, but not in the global deperturbation of the infrared and Raman spectra (Ref. 39). The reported values for the constant  $|K_{2345}|$  obtained from  $l=0$  levels in Refs. 16, 34, 35, 37, 38, and 41 should be divided by  $\sqrt{2}$ , bringing them into agreement with the value of  $|K_{2345}| = 18.28 \text{ cm}^{-1}$  obtained in Refs. 36 and 39 and with an earlier determination that  $|K_{2345}| \approx 20 \text{ cm}^{-1}$  from  $l=1$  levels.<sup>40</sup> No factor of  $\sqrt{2}$  arises for the isolated  $2 \times 2$  resonance between  $(0,0,1,1^{\pm 1},1^{\mp 1})_0^-$  and  $(0,1,0,2^{\pm 2},2^{\mp 2})_0^-$ , which are separated by  $\Delta = 18.14 \text{ cm}^{-1}$  and have nearly identical  $B_v$  values ( $1.1779$  and  $1.1781 \text{ cm}^{-1}$ , respectively).<sup>43</sup> The off-diagonal matrix element (in the parity basis) is  $V_{\text{OD}} = -(K_{2345}/2)$ , so that assuming exact resonance ( $\Delta = 2|V_{\text{OD}}|$ ) yields  $|K_{2345}| = 18.14 \text{ cm}^{-1}$ , in good agreement with  $|K_{2345}| = 18.28 \text{ cm}^{-1}$ . An internally consistent treatment is vitally important here because the transformation from the signed- $l$ -basis to the parity-basis *does not* produce factors of  $\sqrt{2}$  for Fermi resonance between two  $l'' \neq 0$  levels or between two  $l_4 = -l_5 \neq 0$  levels.

A consistent treatment of 2345 resonances in  $(0,0,1,0,0)$ ,  $(0,1,1,0,0)$  and the  $l''=1$  levels  $(0,0,1,1^1,0)^1$  and  $(0,0,1,0,1^1)^1$  has been used to derive  $x_{23}^0$ ,  $x_{34}^0$ , and  $x_{35}^0$  in Ref. 39. This assumes that  $K_{2345}$  depends only weakly on the vibrational quantum numbers. Because the observed 2345 Fermi resonances except for  $(0,0,1,0^0,0^0)_0^- \sim (0,1,0,1^{\pm 1},1^{\mp 1})_0^+$  and  $(0,0,1,1^{\pm 1},1^{\mp 1})_0^- \sim (0,1,0,2^{\pm 2},2^{\mp 2})_0^-$  are complicated by vibrational- $l$ -resonance with unobserved levels, deperturbations to thoroughly check the accuracy to which  $K_{2345}$  is constant are not possible with the available literature data. However, when Fermi resonance and vibrational- $l$ -resonance are treated simultaneously, the constants in Table I and  $|K_{2345}| = 18.28 \text{ cm}^{-1}$  reproduce the vibrational term values for 16 levels in 2345 resonance (listed in Table II of Ref. 16) with a standard deviation of  $1.4 \text{ cm}^{-1}$  and an additional 10 levels in 2345 resonance (from Table 2 of Ref. 43) with a standard deviation of  $2.2 \text{ cm}^{-1}$ .

Finsterhölzl *et al.* noted that the perturbation of the  $2\nu_3''$  level was "only approximately" fit by an assumed 2345 Fermi perturbation.<sup>39</sup> A simple calculation of the relative intensities for the perturbers of  $2\nu_3''$  using the matrix at the bottom of the first column on p. 382 in Ref. 39 (under the likely assumption that the  $2\nu_3''$  basis state carries all the intensity from  $\nu_3''$ ), reveals that the calculated intensities are inconsistent with the intensities subsequently reported in Ref. 16. The reassignment by Smith and Winn<sup>16</sup> of both the  $2\nu_3''$  and  $3\nu_3''$  perturbations from the 2345 Fermi resonance to a new  $2\Delta v_1 = 2\Delta v_2 = -\Delta v_3 = \Delta v_4 = \pm 2$  Fermi resonance is consistent with the intensity data. Furthermore, this reassignment is supported by the negative centrifugal distortion constants  $D'$  observed for the upper partner in each of these perturbations.<sup>44</sup> According to calculations by Bramley *et al.*, the  $2\Delta v_1 = 2\Delta v_2 = -\Delta v_3 = \Delta v_4 = \pm 2$  Fermi resonance is important in both the  $2\nu_3''$  and  $3\nu_3''$  perturbations but the 2345 Fermi resonance should not be neglected.<sup>45</sup>

## V. EXPERIMENT

Stimulated emission pumping (SEP) is a folded variant of optical-optical double resonance. The first laser, named the PUMP, populates a single rovibronic level of an excited electronic state. If a second laser, the DUMP, is tuned through resonance with a transition originating from the level populated by the PUMP and terminating on a vibrational level of the ground electronic state with a smaller (thermal) population, the DUMP stimulates emission to that vibrational level, thereby depopulating the excited electronic state. We detect this depopulation as a decrease in the total intensity of undispersed side fluorescence.

Our fluorescence dip detected SEP experiment is described in detail elsewhere,<sup>46</sup> and will only be outlined here. Briefly, a single 100 Hz repetition rate excimer laser (LAMBDA PHYSIK LPX 210 icc) pumps two tunable dye lasers. The PUMP dye laser (LAMBDA PHYSIK 2002EC with extracavity etalon removed) is frequency doubled in BBO. The doubled light is split by a 222 nm 50% beamsplitter, so that about  $50 \mu\text{J}$  enters identical signal and reference cells containing 200 mTorr acetylene. The doubled PUMP laser ( $0.10 \text{ cm}^{-1}$  resolution) is locked onto a single rotational line of the acetylene  $\tilde{A} \leftarrow \tilde{X}$  transition. Matched photomultipliers detect  $\tilde{A} \rightarrow \tilde{X}$  side fluorescence in both the signal and reference cells. The outputs of the photomultipliers are fed to a fast differential amplifier, which is nulled in the absence of downward transitions. The DUMP dye laser (LAMBDA PHYSIK 3002E) is frequency doubled in BBO. About 20 ns after the PUMP pulse has passed the photomultipliers, between 10 and  $50 \mu\text{J}$  of doubled light counterpropagates along the PUMP beam path in the signal cell. The BBO phase matching angle is continuously optimized by an autotracker as the DUMP laser is scanned. The output of the differential amplifier is detected by a boxcar gated after the DUMP pulse. The signal, a depletion of the side fluorescence in the signal cell as the doubled DUMP laser is scanned across a downward transition, is recorded simultaneously with the molecular iodine absorption spectrum of the DUMP fundamental by a PC. Absolute term values of energy levels are calculated by subtracting the wave number of the SEP transition (obtained by interpolation between iodine lines)<sup>47</sup> from the known term value of the  $\tilde{A}$ -state SEP intermediate.<sup>48</sup> Term value coincidences, discussed in the next section, indicate absolute experimental errors of  $\sigma = 0.020 \text{ cm}^{-1}$ . The error for levels observed by weak transitions may be slightly greater.

## VI. ROTATIONAL ANALYSIS

The rigorous electric dipole  $\Delta J = 0, \pm 1$  ( $J = 0 \nleftrightarrow J = 0$ ) and  $+\leftrightarrow-$  selection rules limit the possible DUMP transitions from a given SEP intermediate level so that comparisons between a few SEP spectra with different SEP intermediate levels can uniquely determine the rotational quantum numbers. Since the levels discussed in this paper (but not all levels observed in this energy region) all appear through nominally allowed transitions, two propen-

TABLE II. Observed term values.<sup>a,b</sup>

$(0,1,0,8^{0,2},0)^{0,2}$	$l=0e$		$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP	Term value	PUMP
$J=0$	6958.034	$R(0)$				
$J=1$	6960.363	$Q(1)$				
$J=2$	6965.109	$Q(2)$	6963.790	$Q(2)$	6963.804	$Q(1)$
	6965.103	$R(0)$	6963.816	$R(0)$	6963.807	$Q(3)$
$J=3$	6972.219	$Q(3)$	6970.862	$Q(3)$	6970.893	$Q(2)$
	6972.199	$R(3)$	6970.837	$R(3)$	6970.856	$Q(4)$
$J=4$	6981.678	$Q(4)$	6980.250	$Q(4)$	6980.359	$Q(3)$
					6980.322	$Q(5)$
					6980.331	$R(3)$
$J=5$	6993.573	$Q(5)$	6991.993	$Q(5)$	6992.146	$Q(4)$
					6992.120	$Q(6)$
$J=6$	7007.852	$Q(6)$	7006.066	$Q(6)$	7006.336	$Q(5)$
					7006.319	$Q(7)$
$J=7$	7024.564	$Q(7)$	7022.467	$Q(7)$	7022.895	$Q(6)$
					7022.882	$Q(8)$
$J=8$	7043.670	$Q(8)$	7041.190	$Q(8)$	7041.825	$Q(7)$
					7041.763	$Q(9)$
$J=9$	7065.157	$Q(9)$	7062.206	$Q(9)$	7063.139	$Q(8)$
$J=10$					7086.786	$Q(9)$

$(0,1,0,6^{2,4},2^{-2})^{0,2}$	$l=0e$		$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP	Term value	PUMP
$J=0$	7020.626	$R(0)$				
$J=1$	7022.962	$Q(1)$				
$J=2$	7027.717	$Q(2)$	7026.002	$Q(2)$	7026.038	$Q(1)$
	7027.742	$R(0)$	7026.042	$R(0)$		
$J=3$	7034.852	$Q(3)$	7033.103	$Q(3)$	7033.081	$Q(2)$
$J=4$	7044.239	$Q(4)$	7042.505	$Q(4)$	7042.567	$Q(3)$
$J=5$	7056.087	$Q(5)$	7054.280	$Q(5)$	7054.338	$Q(4)$
$J=6$	7070.342	$Q(6)$	7068.334	$Q(6)$	7068.530	$Q(5)$
$J=7$	7086.995	$Q(7)$	7084.819	$Q(7)$	7085.067	$Q(6)$
$J=8$	7106.036	$Q(8)$	7103.589	$Q(8)$	7103.956	$Q(7)$
$J=9$	7127.411	$Q(9)$	7124.625	$Q(9)$	7125.284	$Q(8)$
$J=10$	7151.383	$Q(10)$	7148.146	$Q(10)$	7148.872	$Q(9)$

$(0,3,0,2^{0,2},0)^{0,2}$	$l=0e$		$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP	Term value	PUMP
$J=0$	7034.642	$R(0)$				
$J=1$	7037.000	$Q(1)$				
$J=2$	7041.619	$Q(2)$	7038.731	$Q(2)$	7038.714	$Q(1)$
	7041.612	$R(0)$	7038.738	$R(0)$		
$J=3$	7048.586	$Q(3)$	7045.668	$Q(3)$		
$J=4$	7057.823	$Q(4)$	7054.962	$Q(4)$		
$J=5$	7069.445	$Q(5)$	7066.512	$Q(5)$		
$J=6$	7083.326	$Q(6)$	7080.395	$Q(6)$		
$J=7$	7099.613	$Q(7)$	7096.675	$Q(7)$		
$J=8$	7118.188	$Q(8)$	7115.188	$Q(8)$		
$J=9$	7139.067	$Q(9)$	7135.994	$Q(9)$	7136.136	$Q(8)$
$J=10$	7162.420	$Q(10)$				

$(0,1,0,6^{2,2},2^0)^2$	$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP
$J=2$	7072.212	$R(0)$	7072.272	$Q(1)$
$J=3$	7079.327	$Q(3)$		
	7079.335	$R(1)$		
$J=4$	7088.746	$Q(4)$	7088.777	$Q(3)$
$J=5$	7100.560	$Q(5)$		
$J=6$	7114.700	$Q(6)$		
$J=8$	7150.211	$Q(8)$		
$J=9$	7171.401	$Q(9)$		
$J=10$	7195.149	$Q(10)$		
$J=11$	7221.101	$Q(11)$		

TABLE II. (Continued.)

$(0,0,1,5^{1,3},1^{-1})^{0,2}$	$l=0e$		$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP	Term value	PUMP
$J=0$	7081.313	$R(0)$				
$J=1$	7083.716	$Q(1)$				
	7083.696	$R(1)$				
$J=2$	7088.433	$Q(2)$	7083.045	$R(0)$	7083.081	$Q(1)$
	7088.414	$R(0)$				
$J=3$	7095.496	$Q(3)$	7090.110	$R(1)$		
$J=4$	7104.938	$Q(4)$	7099.565	$Q(4)$		
$J=5$	7116.730	$Q(5)$	7111.325	$Q(5)$		
$J=6$	7130.836	$Q(6)$	7125.481	$Q(6)$		
$J=7$	7147.424	$Q(7)$	7141.972	$Q(7)$		
$J=8$	7166.337	$Q(8)$	7160.863	$Q(8)$		
$J=9$	7187.546	$Q(9)$				
$J=10$	7211.286	$Q(10)$	7205.553	$Q(10)$		
$J=11$	7237.272	$Q(11)$	7231.420	$Q(11)$		

$(0,0,1,5^1,1^1)^2$	$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP
$J=2$	7101.862	$Q(2)$	7101.893	$Q(1)$
	7101.860	$R(0)$		
$J=3$	7108.954	$Q(3)$	7108.942	$Q(2)$
$J=4$	7118.344	$Q(4)$	7118.381	$Q(3)$
$J=5$	7130.112	$Q(5)$	7130.145	$Q(4)$
$J=6$			7144.228	$Q(5)$
$J=7$	7160.679	$Q(7)$		
$J=8$	7179.465	$Q(8)$		
$J=10$	7224.124	$Q(10)$		
$J=11$	7249.932	$Q(11)$		

$(0,1,0,6^0,2^{0,2})^{0,2}$	$l=0e$		$l=2e$		$l=2f$	
	Term value	PUMP	Term value	PUMP	Term value	PUMP
$J=0$	7120.763	$R(0)$				
$J=1$	7123.115	$Q(1)$				
$J=2$	7127.835	$Q(2)$	7129.912	$Q(2)$	7129.890	$Q(1)$
	7127.839	$R(0)$	7129.937	$R(0)$		
$J=3$	7134.921	$Q(3)$	7136.958	$Q(3)$	7136.984	$Q(2)$
					7137.018	$Q(4)$
$J=4$	7144.323	$Q(4)$	7146.407	$Q(4)$	7146.370	$Q(3)$
					7146.401	$Q(5)$
$J=5$	7156.144	$Q(5)$	7158.244	$Q(5)$	7158.182	$Q(4)$
$J=6$	7170.309	$Q(6)$	7172.432	$Q(6)$	7172.391	$Q(5)$
$J=7$	7186.805	$Q(7)$	7188.989	$Q(7)$	7188.897	$Q(6)$
$J=8$	7205.680	$Q(8)$	7207.945	$Q(8)$	7207.814	$Q(7)$
					7207.758	$Q(9)$
$J=9$	7226.814	$Q(9)$	7229.166	$Q(9)$	7229.056	$Q(8)$
					7229.094	$Q(10)$
$J=10$	7250.409	$Q(10)$	7252.941	$Q(10)$	7252.613	$Q(9)$
$J=11$	7276.283	$Q(11)$			7278.605	$Q(10)$

\*Rovibrational term values are reported in  $\text{cm}^{-1}$ . The experimental uncertainty ( $1\sigma$ ) is  $\pm 0.020 \text{ cm}^{-1}$ .

<sup>b</sup>The rotational line of the  $\tilde{A}(0,0,2,0,0)^1 \leftarrow \tilde{X}(0,0,0,0,0)^0$  PUMP transition used to obtain each term value is listed in the column labeled PUMP.

sity rules further simplify the rotational assignment process. The  $\tilde{A}-\tilde{X}$  electric dipole transition moment of acetylene is perpendicular to the plane of the *trans*-bent  $\tilde{A}$  state, giving rise to  $\Delta K \equiv K' - l'' = \pm 1$  rotational propensity rules. The vibrational propensity rule for electronic transitions prohibits a change of vibrational symmetry in the common  $C_{2h}$  subgroup of the  $\tilde{A}$  and  $\tilde{X}$  symmetry groups. Thus transitions to  $\Sigma_g^+$  ( $l''=0$ ) and  $\Delta_g$  ( $l''=2$ ) vibrational states are allowed from the rotational levels of

the  $\tilde{A}2\nu_3K'=1$  state used as SEP intermediates, and all other transitions are *nominally* forbidden. Note that a “rotational” propensity rule serves to restrict the  $\tilde{X}$ -state “vibrational” levels accessible from a given  $\tilde{A}$ -state  $K'$  level.

In the SEP experiments, the initial vibrational level was always the zero point level of the ground electronic state, so that all initial rotational levels have *e* parity. Therefore, double resonance transitions of the type  $QQ$ ,  $RR$ , and  $RP$  terminate on *e* parity levels and double reso-

nance transitions of the type  $QR$ ,  $QP$ , and  $RQ$  terminate on  $f$  parity levels. Rotational assignments at low  $J$  were secured by comparing the energy levels observed in  $R(0)$ ,  $Q(1)$ , and  $Q(2)$  PUMPed SEP spectra.  $J''=2$ ,  $l''=2e$  and  $J''=2$ ,  $l''=0$  levels are the only allowed transitions that occur in *both*  $R(0)$  and  $Q(2)$  PUMPed SEP spectra, so that a level detected in both spectra must belong to one of these two possibilities. Since the  $\bar{A}$ -state rotational level reached by  $Q(2)$  lies energetically above the  $\bar{A}$ -state rotational level reached by  $R(0)$ , the term value coincidence also proves that the double resonance transitions are downward (stimulated emission by the DUMP) rather than upward (absorption of the DUMP). All  $J''=2$ ,  $l''=2e$  levels have been identified by their experimentally exact degeneracy with the  $J''=2$ ,  $l''=2f$  component which appears in  $Q(1)$  PUMPed SEP spectra.<sup>49</sup>

If the vibrational levels are widely spaced, the remaining noncoincident level in each of these three SEP spectra [ $Q(1)$ ,  $Q(2)$  and  $R(0)$  PUMPed] can then be unambigu-

ously rotationally assigned: the remaining level in the  $R(0)$  spectrum is  $J''=0$ ,  $l''=0$ ; the remaining level in the  $Q(1)$  spectrum is  $J''=1$ ,  $l''=0$ ; and the remaining level in the  $Q(2)$  spectrum is  $J''=3$ ,  $l''=2f$ . An immediate check of the consistency of the rotational assignment can be made by verifying that the three  $l''=0$  levels follow the energy level formula  $E=T_0+BJ(J+1)$  and that the two  $l''=2f$  levels have the same rotational constant as the three  $l''=0$  levels. A comparison of the relative intensities in each of the three spectra to rotational intensity calculations provides a second check. Higher  $J$  levels were assigned similarly by term value coincidences, extrapolation, and rotational intensities, and term values for all allowed rotational transitions are listed in Table II.

Excited bending levels which differ only by  $|\Delta l_t|=2$  perturb each other by the  $J$ -dependent rotational- $l$ -resonance interaction. In the signed- $l$ -basis, the off-diagonal matrix elements for rotational- $l$ -resonance are

$$\langle v_t^{l_t}; J, l_t | \mathcal{H} | v_t^{l_t \pm 2}; J, (l_t \pm 2) \rangle = \frac{1}{2} q_t \sqrt{(v_t \mp l_t)(v_t \pm l_t + 2)} \sqrt{[J(J+1) - l(l \pm 1)][J(J+1) - (l \pm 1)(l \pm 2)]}. \quad (13)$$

Although  $q_4$  and  $q_5$  are quite small, approximately  $5 \times 10^{-3} \text{ cm}^{-1}$ , the explicit and roughly linear dependence of the off-diagonal matrix element in Eq. (13) on  $v_t$  (for  $v_t \gg l_t$ ) makes the effects of rotational- $l$ -resonance quite substantial for the high  $v_t''$  levels studied here. The magnitude of the rotational- $l$ -resonance is particularly useful for making vibrational assignments, because it is a direct measure of bending excitation. For rotational- $l$ -resonance between an  $l''=0, 2$  pair, the off-diagonal matrix elements between  $\Sigma^+ l''=0$  levels and the  $e$  parity components of  $l''=2$  levels, have the form

$$V = Q_v \sqrt{J(J+1)[J(J+1) - 2]} \quad (14)$$

in the parity basis. If either  $l_4$  or  $l_5$  is zero for both the  $l''=0$  and the  $l''=2$  state, then

$$Q_v = \frac{\sqrt{2}}{4} q_t \sqrt{(v_t - l_t)(v_t + l_t + 2)}, \quad (15)$$

where the subscript  $t$  refers to the bending normal mode for which the vibrational angular momentum increases by two units. Equation (15) is obtained by transforming Eq. (13) from the signed- $l$ -basis to the parity basis. Note that all  $l=2f$  components are unperturbed by  $\Sigma^+ l=0$  levels and are thus particularly useful in estimating the rotational constant,  $B_v$ .<sup>50</sup> We have fit the observed  $l=0$  and 2 rotational energy levels to effective Hamiltonians with off-diagonal matrix elements of the form given by Eq. (14). To prevent rotational- $l$ -resonance between the observed  $l=2$  levels and unobserved  $l=4$  levels from distorting the least squares fits, least squares weights ( $w=1/s^2$ ) for  $J \geq 4$  levels are calculated from errors due to both experimental error and model error if  $v_4 \geq 4$ . The model error is calculated from second order perturbation theory as  $V^2/\Delta E$

where  $V$  is calculated from Eq. (13) and  $\Delta E = 12g_{44}^0$ . With the exception of the rotational constant for the  $l=0, 2$  pair near  $7020 \text{ cm}^{-1}$  [where  $B_v = 1.1813(4)$  without model error], the introduction of a model error in the least squares fits does not significantly affect the spectroscopic constants. Vibrational band origins,  $G_v$ , rotational constants,  $B_v$ , and rotational- $l$ -resonance matrix elements,  $Q_v$  [defined by Eq. (14)], are listed in Table III for all observed transitions.

## VII. VIBRATIONAL ANALYSIS

All  $\Sigma_g^+$  vibrational levels predicted to lie within  $200 \text{ cm}^{-1}$  of the region sampled by SEP are listed in Table III along with their zero-order rotational constants predicted from Eq. (5). Combination states  $nv_2'' + 2mv_4''$  are expected to be Franck-Condon bright due to the large change in geometry along the CC stretch and *trans*-bend coordinates on  $\bar{A} \rightarrow \bar{X}$  emission from  $K'=1$ . (The restriction to even quanta of the *trans*-bend arises from the  $\Delta K = \pm 1$  "rotational" propensity rule.) When we began this analysis, we thought it possible that states with one or two quanta of  $v_1''$ , the symmetric CH stretch, would also be Franck-Condon bright by analogy to the  $\bar{A} \leftarrow \bar{X}$  absorption spectrum.<sup>21</sup> It will be shown below (Sec. X) that this is not so. The rotational constant confirms the assignment of the dispersed fluorescence feature at  $G_v = 6957 \text{ cm}^{-1}$  to the Franck-Condon bright state (0,1,0,8,0). The assignment of the  $l''=0, 2$  pair seen in the SEP spectrum at  $7030 \text{ cm}^{-1}$  to the Franck-Condon bright state (0,3,0,2,0) is also obvious based on the vibrational band origin and rotational constant. Based only on the rotational constant and term value for the  $7120 \text{ cm}^{-1}$  state, either a possibly Franck-

TABLE III. Band origins, rotational constants, and assignments.<sup>a</sup>

Band origin	$l''$	$B_v$	$Q_v \times 10^3$	$(v_1, v_2, v_3, v_4^k, v_5^l)^l$	$B_v^0$
7122.81(2)	2	1.1803(4) <sup>b</sup>		(0106 <sup>0</sup> 2 <sup>2</sup> ) <sup>2</sup>	1.1824(2)
7120.75(1)	0		+6.8(12)	(0106 <sup>0</sup> 2 <sup>0</sup> ) <sup>0</sup>	
7094.86(2)	2	1.1750(4)		(0015 <sup>1</sup> 1 <sup>1</sup> ) <sup>2</sup>	1.1794(2)
7081.33(2)	0		$\pm 8.3(15)^c$	(0015 <sup>1</sup> 1 <sup>-1</sup> ) <sup>0</sup> <sub>+</sub>	1.1794(2)
7075.98(2)	2	1.1793(4) <sup>b</sup>		(0015 <sup>3</sup> 1 <sup>-1</sup> ) <sup>2</sup> <sub>+</sub>	
7065.13(4)	2	1.1816(6)		(0106 <sup>2</sup> 2 <sup>0</sup> ) <sup>2</sup>	1.1824(2)
7034.64(2)	0		$\pm 6.8(10)^c$	(0302 <sup>0</sup> 0 <sup>0</sup> ) <sup>0</sup>	1.1606(2)
7031.76(3)	2	1.1595(4) <sup>b</sup>		(0302 <sup>2</sup> 0 <sup>0</sup> ) <sup>2</sup>	
7020.62(2)	0		+12.5(7)	(0106 <sup>2</sup> 2 <sup>-2</sup> ) <sup>0</sup> <sub>+</sub>	1.1824(2)
7018.94(2)	2	1.1807(5) <sup>b</sup>		(0106 <sup>4</sup> 2 <sup>-2</sup> ) <sup>2</sup>	
6958.01(1)	0		+15.0(5)	(0108 <sup>0</sup> 0 <sup>0</sup> ) <sup>0</sup>	1.1807(2)
6956.71(1)	2	1.1811(4) <sup>b</sup>		(0108 <sup>2</sup> 0 <sup>0</sup> ) <sup>2</sup>	

<sup>a</sup>Fitted constants differ slightly from those reported in Ref. 19 due to inclusion of more SEP data and use of more accurate  $A$ -state term values from Ref. 48. Numbers in parentheses are  $2\sigma$  errors (in the last reported digit) from the least squares fits. All molecular constants are in  $\text{cm}^{-1}$ .

<sup>b</sup>Fitted rotational constants for  $l''=0$  and 2 components were constrained to be equal.

<sup>c</sup>Intensity interference effects were too weak to experimentally determine the signs of the rotational- $l$ -resonance constants for the (0,0,1,5,1) and (0,3,0,2,0) levels.

*Condon bright (1,0,0,6,0) level or the nominally dark (0,1,0,6,2) level [appearing through DD resonance with (0,1,0,8,0)] is a plausible assignment.* The rotational constant for the levels at  $7020 \text{ cm}^{-1}$  is slightly larger than that for the  $7120 \text{ cm}^{-1}$  levels [the agreement within experimental error with the zero-order rotational constant for (0,1,0,6,2) reported in Ref. 19 was apparently fortuitous], which suggests that at least one member of the (0,1,0,6,2) set of *cis*-bend excited levels is present since (1,0,0,6,0) can account for at most one of the two pairs of levels.

The key to the vibrational assignment is the detection and identification of two more  $l''=2$  levels than  $l''=0$  levels (the  $e$  and  $f$  parity components of an  $l''=2$  level are not counted separately). If only one degenerate bending vibration is excited, the number of observed  $l''=0$  levels

must equal or exceed the number of  $l''=2$  levels. Since the rotational intensity factors are stronger for transitions to  $l''=0$  levels from the  $\tilde{A}^1A_u K'=1$  intermediates used in the SEP experiment, the observation of "extra"  $l''=2$  levels is strong evidence that combination levels with simultaneous excitation of both the *trans* and *cis* degenerate bending vibrations appear in the spectrum. However, the (0,1,0,6,2) set of levels, consisting of (0,1,0,6 <sup>$\pm 2$</sup> ,2 <sup>$\mp 2$</sup> )<sup>0</sup>, (0,1,0,6<sup>0</sup>,2<sup>0</sup>)<sup>0</sup>, (0,1,0,6<sup>2</sup>,2<sup>0</sup>)<sup>2</sup>, (0,1,0,6<sup>0</sup>,2<sup>2</sup>)<sup>2</sup>, and (0,1,0,6<sup>4</sup>,2<sup>-2</sup>)<sup>2</sup> levels, yields only one extra  $l''=2$  level.

TABLE IV. Zero order term values [from Eq. (3)] and rotational constants for  $\Sigma_g^+$  states calculated to lie in the  $6700\text{--}7300 \text{ cm}^{-1}$  region.

$v_1$	$v_2$	$v_3$	$v_4$	$l_4$	$v_5$	$l_5$	$G_v^0/(\text{cm}^{-1})$	$B_v^0/(\text{cm}^{-1})$
0	0	0	4	2	6	-2	6709.42	1.1947
0	0	0	4	0	6	0	6718.59	1.1947
1	1	0	0	0	2	0	6758.73	1.1678
0	2	0	0	0	4	0	6800.62	1.1728
0	0	0	2	2	8	-2	6866.62	1.1964
0	0	0	2	0	8	0	6875.78	1.1964
0	1	0	8	0	0	0	6943.86	1.1807
0	3	0	2	0	0	0	7034.10	1.1606
1	0	0	6	0	0	0	7044.44	1.1775
0	0	0	0	0	10	0	7058.20	1.1981
0	1	0	6	2	2	-2	7072.31	1.1824
0	0	1	5	1	1	-1	7079.83	1.1796
0	1	0	6	0	2	0	7081.48	1.1824
1	0	0	4	2	2	-2	7194.81	1.1792
1	0	0	4	0	2	0	7203.98	1.1792
0	1	0	4	4	4	-4	7207.65	1.1842
0	0	1	3	3	3	-3	7220.73	1.1813
0	1	0	4	2	4	-2	7235.15	1.1842
0	0	1	3	1	3	-1	7239.07	1.1813
0	1	0	4	0	4	0	7244.32	1.1842
1	2	0	0	0	0	0	7281.49	1.1573

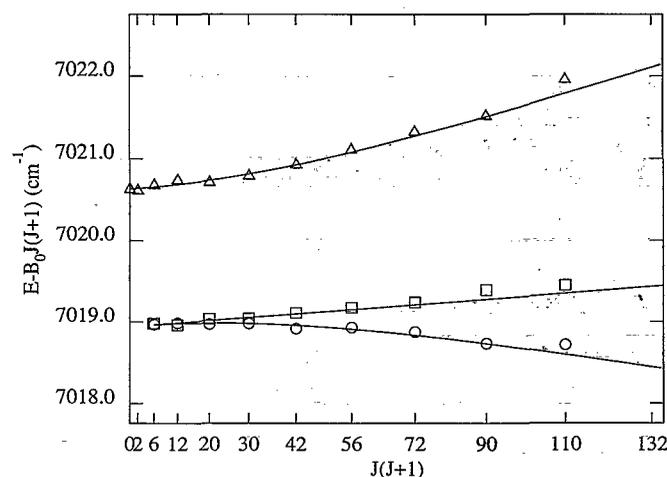


FIG. 1. Reduced rotational term value plot for the  $(0,1,0,6^{2,4},2^{-2})^{0,2}$  levels. Rovibrational term values  $E$  are reduced by subtracting  $B_0 J(J+1)$  and plotted against  $J(J+1)$  to highlight differences between vibrational levels. Triangles represent  $l=0$  levels, circles represent  $l=2e$  parity levels, and squares represent  $l=2f$  parity levels. Experimental error bars are approximately the size of the symbols representing the data. The rotational constant may be obtained from the slope of the line passing through the  $l=2f$  parity levels, and the positive slope indicates substantial bend excitation. The large hyperbolic variation with  $J(J+1)$  of the splitting between  $l=0$  levels and  $l=2e$  parity levels measures the rotational- $l$ -resonance interaction, indicating that the  $l=0$  and  $l=2$  levels differ by 2 quanta of vibrational angular momentum in a highly excited bending mode.

The observation of two "extra"  $l''=2$  levels is strong evidence that *another* set of nominally dark levels with simultaneous excitation of both the *trans* and *cis* degenerate bending vibrations also appears in the spectrum.

From Table IV, the (0,1,0,6,2) and (0,0,1,5,1) sets of levels are the only sets with simultaneous excitation in both *trans* and *cis*-bending predicted to lie within  $100\text{ cm}^{-1}$  of the observed levels. (0,0,1,5,1) has *one*  $\Sigma_g^+$   $l''=0$  sublevel,  $(0,0,1,5^{\pm 1}, 1^{\mp 1})_+^0$ , and *two*  $l''=2$  sublevels,  $(0,0,1,5^1, 1^1)^2$  and  $(0,0,1,5^3, 1^{-1})^2$ , which can steal intensity from (0,1,0,6,2) via the well characterized  $\Delta v_3 = -\Delta v_2 = -\Delta v_4 = -\Delta v_5 = \pm 1$ ,  $\Delta l_4 = -\Delta l_5 = \pm 1$  "2345" Fermi resonance which perturbs the  $\nu_3'$  fundamental.<sup>39</sup> Together, the (0,1,0,6,2) and (0,0,1,5,1) sets of levels can account for two extra  $l''=2$  levels. We have assigned the level at  $7081\text{ cm}^{-1}$  as  $(0,0,1,5^{\pm 1}, 1^{\mp 1})_+^0$  based on the vibrational band origin and rotational constant. The (0,0,1,5,1) and (0,1,0,6,2) groups account for *all* of the remaining SEP transitions in Table III.

For the levels (0,1,0,8,0) and (0,3,0,2,0) the level shifts due to rotational- $l$ -resonance can be accurately predicted by a slight refinement of Pliva's spectroscopic constants.<sup>22</sup> An intensity interference effect between  $l''=0$  and  $l''=2e$  levels has allowed us to determine independently that the rotational- $l$ -resonance matrix elements are also positive, as predicted, for the  $6958\text{ cm}^{-1}$  levels (the interference effect is too weak to observe for the  $7034\text{ cm}^{-1}$  levels).<sup>46</sup> Since we can predict both the magnitude and sign of rotational- $l$ -resonance matrix elements for levels not involved in vibration- $l$ -resonance, we have confidence they are a reliable diagnostic for vibrational assignment. Even for levels involved in vibrational- $l$ -resonance, the magnitude of the rotational- $l$ -resonance constant  $Q_v$  often suggests assignment of the change in  $l''$  between  $l''=0$  and  $l''=2$  as predominantly due to  $l_4''$  or  $l_5''$ . For instance, the rotational- $l$ -resonance for the (0,1,0,6,2) levels at  $7020\text{ cm}^{-1}$  indicates a  $|\Delta l_4''| = 2$  interaction. The explicit  $v_4'', v_5''$  scaling of these interaction matrix elements is of both diagnostic and dynamical importance.

In particular, the rotational- $l$ -resonance interaction constant between the  $l''=0$  and  $l''=2$  levels at  $7120\text{ cm}^{-1}$  is only half the  $Q_v$  expected for a  $\Delta l_4=2$  interaction with  $v_4'' = 6$ , conclusively ruling out the (1,0,0,6,0) CH stretch

assignment for this level. Since  $v_4'' = 6$  and  $v_5'' = 0$  for the (1,0,0,6,0) assignment, the  $\Delta l_4=2$  rotational- $l$ -resonance with  $v_4'' = 6$  should be quite large, similar to that in the levels near  $7020.53\text{ cm}^{-1}$ . Instead, the rotational- $l$ -resonance is quite small, similar to that in the levels  $(0,3,0,2,0)^{0,2}$ , near  $7034.59\text{ cm}^{-1}$ , which have  $\Delta l_4=2$  with  $v_4'' = 2$ . Since  $v_4'' = 6$  and  $v_5'' = 2$  for the (0,1,0,6,2) assignment, the (0,1,0,6,2) assignment allows a small  $\Delta l_5=2$  rotational- $l$ -resonance similar to that in (0,3,0,2,0); i.e., the  $\nu_5$   $l$ -resonance in (0,1,0,6,2) can be smaller by a factor of  $q_5^0 \sqrt{2} \times 4 / q_4^0 \sqrt{6} \times 8$  than the  $\nu_4$   $l$ -resonance in (1,0,0,6,0). Comparisons of the reduced term plots for  $(0,3,0,2,0)$ ,  $(0,1,0,6^{\pm 2, \pm 4}, 2^{\mp 2})^{0,2}$ ,  $(0,1,0,6^0, 2^{0, \pm 2})^{0,2}$  in Figs. 1, 2, and 3 or the  $Q_v$  in Table III are quite convincing evidence for the (0,1,0,6,2) assignment. *The small rotational- $l$ -resonance at  $7120\text{ cm}^{-1}$  and the two extra  $l=2$  levels produced by vibrational- $l$ -resonance prove the combined  $\nu_3/\nu_5$  assignment proposed here.*

We give the matrices describing the vibrational interactions among the observed levels below. The  $l''=0$  matrix has been simplified by transforming it to the parity basis, where it splits into  $\Sigma_g^+$  and  $\Sigma_g^-$  blocks. The  $\Sigma_g^+$  and  $\Sigma_g^-$  blocks are coupled to the  $l''=2e$  and  $f$  blocks, respectively, by rotational- $l$ -resonance, but we have effectively treated this interaction separately in our preliminary fits. It must be kept in mind that the observed levels are coupled to unobserved states by the same set of interactions given by Eqs. (6)–(9). For example, the (0,1,0,6,2) levels are coupled to (0,1,0,4,4) levels by DD resonance, the (0,1,0,4,4) levels are coupled to (0,0,1,3,3) by Fermi resonance, and the (0,0,1,5,1) levels are also coupled to (0,0,1,3,3) by DD resonance. All the above groups of levels have vibrational- $l$ -doubling and resonance interactions and are further coupled by Fermi and DD resonance to other unobserved levels. To lowest order, the constants  $K_{2345}$ ,  $s_{45}$ , etc. coupling the unobserved levels by Eqs. (6)–(9) are identical with those coupling the observed levels, and are assumed here to have the same magnitude. The slight differences which arise in higher orders of perturbation theory have been discussed by Pliva<sup>22</sup> and Herman and co-workers.<sup>33</sup>

The  $l''=0$ ,  $\Sigma_g^+$  block is

$$\begin{vmatrix} (0,1,0,6^0, 2^0)^0 & 4\sqrt{3}r_{45} & -\sqrt{6}K_{2345}/4 & 4s_{45} \\ 4\sqrt{3}r_{45} & (0,1,0,6^{\pm 2}, 2^{\mp 2})^0 & -K_{2345}/\sqrt{2} & \sqrt{3}(r_{45} + 2g_{45}) \\ -\sqrt{6}K_{2345}/4 & -K_{2345}/\sqrt{2} & (0,0,1,5^{\pm 1}, 1^{\mp 1})^0 + 3r_{45} & 0 \\ 4s_{45} & \sqrt{3}(r_{45} + 2g_{45}) & 0 & (0,1,0,8^0, 0^0)^0 \end{vmatrix}.$$

The  $l''=0$ ,  $\Sigma_g^-$  block is

$$\begin{vmatrix} (0,1,0,6^{\pm 2}, 2^{\mp 2})^0 & -K_{2345}/\sqrt{2} \\ -K_{2345}/\sqrt{2} & (0,0,1,5^{\pm 1}, 1^{\mp 1})^0 - 3r_{45} \end{vmatrix}.$$

The  $l''=2$  matrix is

$$\begin{vmatrix}
 (0,1,0,6^0,2^2)^2 & 2\sqrt{6}r_{45} & 0 & -\sqrt{6}K_{2345}/4 & 0 & \sqrt{10}(r_{45}+2g_{45})/2 \\
 2\sqrt{6}r_{45} & (0,1,0,6^2,2^0)^2 & 2\sqrt{5}r_{45} & -K_{2345}/2 & -\sqrt{2}K_{2345}/4 & \sqrt{15}s_{45} \\
 0 & 2\sqrt{5}r_{45} & (0,1,0,6^4,2^{-2})^2 & 0 & -\sqrt{10}K_{2345}/4 & \sqrt{3}(r_{45}+2g_{45})/2 \\
 -\sqrt{6}K_{2345}/4 & -K_{2345}/2 & 0 & (0,0,1,5^1,1^1)^2 & \sqrt{8}r_{45} & 0 \\
 0 & -\sqrt{2}K_{2345}/4 & -\sqrt{10}K_{2345}/4 & \sqrt{8}r_{45} & (0,0,1,5^3,1^{-1})^2 & 0 \\
 \sqrt{10}(r_{45}+2g_{45})/2 & \sqrt{15}s_{45} & \sqrt{3}(r_{45}+2g_{45})/2 & 0 & 0 & (0,1,0,8^2,0^0)^2
 \end{vmatrix}$$

The overall pattern of energy levels is qualitatively consistent with diagonalization of a complete Fermi/DD/vibrational- $l$ -resonance Hamiltonian (including *all* coupled levels, not just the observed levels) using literature values for the Fermi-resonance<sup>39</sup> and vibrational- $l$ -resonance constants<sup>22</sup> and a Darling–Dennison constant  $|s_{45}| \approx 10 \text{ cm}^{-1}$  deduced from the dispersed fluorescence intensities.<sup>15</sup> The vibrational couplings between the observed  $l''=0$  levels are diagrammed in detail in Fig. 2 of Ref. 19. All  $l''=0$  levels interacting with the observed levels by the resonances discussed here are shown schematically in Fig. 4. In these calculations, the levels assigned as  $(0,1,0,6,2)$  at  $7120$  and  $7020 \text{ cm}^{-1}$  correlate to unperturbed  $(0,1,0,6^0,2^{0,2})^{0,2}$  and  $(0,1,0,6^{2,4},2^{-2})^{0,2}$  basis states, respectively, although the  $l_4/l_5$  labels lose some of their meaning due to the vibrational- $l$ -resonance. This mixing of the  $l_4/l_5$  labels may explain why the rotational- $l$ -resonance constants for the  $(0,1,0,6,2)$  levels differ somewhat from those predicted by Eq. (13) and Eq. (15).

### VIII. VIBRATIONAL DEPENDENCE OF $g_{44}$

The effective  $g_{44}$  constant which determines the  $l''=0,2$  splitting for a level with no *cis*-bend excitation is given by

$$g_{44,\text{eff}} = g_{44}^0 + \sum_i y_i^{44} v_i + \dots \quad (16)$$

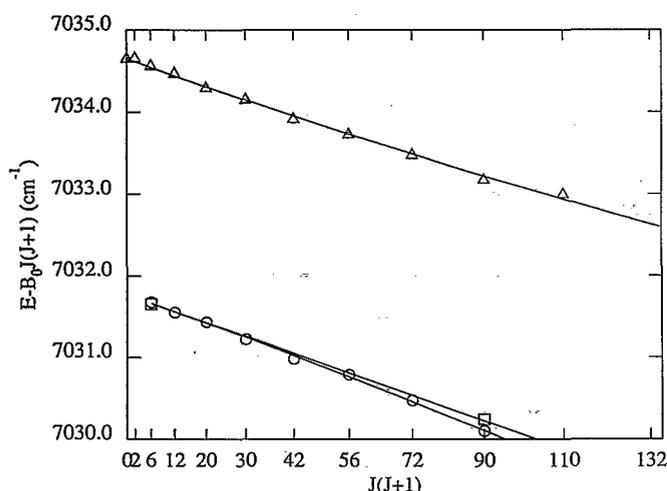


FIG. 2. Reduced rotational term value plot for the  $(0,3,0,2,0)$  levels. The negative slope indicates substantial stretching excitation. Note the small rotational- $l$ -resonance interaction characteristic of 2 bending quanta.

The constants  $g_{44}^0$ ,  $y_4^{44}$ , and  $y_5^{44}$  have been determined by Pliva<sup>22</sup> and Kabbadj *et al.*,<sup>33</sup> although  $y_4^{44}$  is not well determined. The  $g_{44,\text{eff}}$  constants for the  $(0,1,0,8,0)$ ,  $(0,2,0,5,0)$ , and  $(0,3,0,2,0)$  levels observed by SEP decrease linearly, as expected from Eq. (14).<sup>19</sup> Although it is possible that the  $l''=0,2$  splitting for  $(0,1,0,8,0)$  is perturbed by the interaction with the  $(0,1,0,6,2)$  set of levels, the splittings within  $(0,2,0,5,0)$  and  $(0,3,0,2,0)$  will not be substantially affected by DD resonance because the energy gaps are larger and the off-diagonal matrix elements are smaller. Thus it seems reasonable to use these levels, in combination with the known  $l''=0,2$  splitting for  $(0,0,0,2,0)$ , to determine  $g_{44}^0$ ,  $y_2^{44}$ , and  $y_4^{44}$ . We obtain  $g_{44}^0 = 0.73 \text{ cm}^{-1}$ ,  $y_2^{44} = -0.12 \text{ cm}^{-1}$ , and  $y_4^{44} = 0.03 \text{ cm}^{-1}$ . This value of  $y_2^{44}$  is twice as large as any correction due to the bending vibrations.

These constants predict  $g_{44,\text{eff}} = 0.55 \text{ cm}^{-1}$  for the level  $(0,3,0,6,0)$  reported by Abramson *et al.*<sup>18</sup> Using the  $\tilde{A}(0,0,3,0,0) \leftarrow \tilde{X}(0,0,0,0,0) \nu_{Q_0}(5)$  PUMP transition, levels assigned as  $J''=4$ ,  $l''=2 f$  ( $9467.03 \text{ cm}^{-1}$ ),  $J''=5$ ,  $l''=2e$  ( $9478.61 \text{ cm}^{-1}$ ),  $J''=5$ ,  $l''=0$  ( $9481.14 \text{ cm}^{-1}$ ),

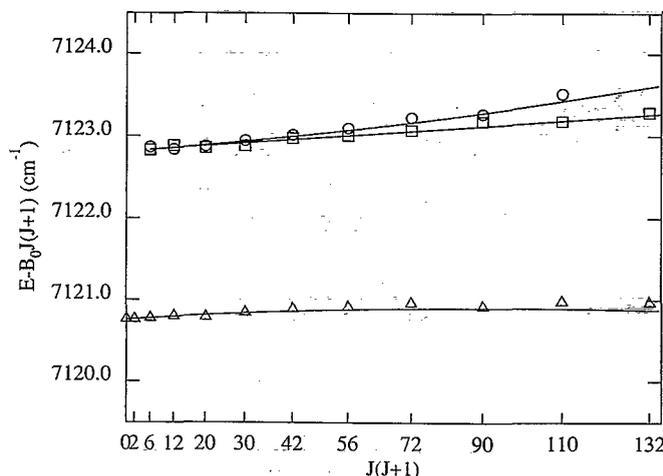


FIG. 3. Reduced rotational term value plot for the  $7120 \text{ cm}^{-1}$  levels. As in Fig. 1, the positive slope indicates substantial bending excitation but the small rotational- $l$ -resonance interaction resembles that in Fig. 2, indicating little excitation in the bending mode for which  $l$  changes. Both observations can be explained by the  $(0,1,0,6^0,2^{0,2})^{0,2}$  assignment.

$J''=6, l''=2 f$  (9492.60  $\text{cm}^{-1}$ ) were observed under the (0,3,0,6,0) dispersed fluorescence peak.<sup>18</sup> The rotational constant  $B_v \approx 1.162(3)$  can be estimated from the separation between  $J''=4, l''=2 f$  and  $J''=6, l''=2 f$ , since the  $f$  parity component of  $l''=2$  does not interact with  $l''=0$  and the interaction with  $l''=4f$  will be weak. This estimate agrees within error with the zero-order  $B_v=1.1655(2)$   $\text{cm}^{-1}$  predicted by Eq. (5). The observed splitting between  $J''=5, l''=0$  and  $J''=5, l''=2e$  is  $-2.53(3)$   $\text{cm}^{-1}$ , some of which is due to rotational- $l$ -resonance and some of which is due to  $g_{44, \text{eff}}$ . Using Eq. (13) and the literature<sup>33</sup> value for  $q_4$ , we expect an off-diagonal matrix element of 0.371  $\text{cm}^{-1}$  between  $J''=5, l''=2e$  and  $J''=5, l''=0$ . We may use this matrix element and the observed splitting to obtain a deperturbed splitting of  $-2.42$   $\text{cm}^{-1} = (g_{44, \text{eff}} - B_v)l^2$ , yielding  $g_{44, \text{eff}} = 0.557(7)$   $\text{cm}^{-1}$ , in excellent agreement with our predicted value. Since the rotational term values for the  $J''=5$  levels (in addition to the splitting) are predicted accurately, we list the band origins:  $G_v(l''=2) = 9443.79(90)$   $\text{cm}^{-1}$  and  $G_v(l''=0) = 9446.21(90)$   $\text{cm}^{-1}$ . Similarly, the two  $Q(3)$  transitions in Fig. 5(b) of Ref. 15 are split by  $-2.02(3)$   $\text{cm}^{-1}$ , yielding  $g_{44, \text{eff}} = 0.68$   $\text{cm}^{-1}$  if  $B_v=1.18$   $\text{cm}^{-1}$  is assumed, in agreement with the predicted value of  $g_{44, \text{eff}} = 0.67$   $\text{cm}^{-1}$  for the (0,2,0,6,0) level from Eq. (14). The large effect of CC stretch excitation on the  $l$  splitting is thus confirmed by observations on five different highly excited levels, (0,1,0,8,0), (0,2,0,5,0), (0,2,0,6,0), (0,3,0,2,0), and (0,3,0,6,0). *This is the first observation of a systematic effect due to stretching vibration on the  $l$ -splitting constants for acetylene.*

Rao and co-workers<sup>51</sup> have observed appreciable ( $\approx 1$   $\text{cm}^{-1}$ ) splittings between two pairs of transitions in the 1.5  $\mu$  region:  $(1,0,1,0,2^2)^2 \leftarrow (0,0,0,0,2^2)^2$  and  $(1,0,1,0,2^0)^0 \leftarrow (0,0,0,0,2^0)^0$ ;  $(1,0,1,2^0,2)^2 \leftarrow (0,0,0,2^2,0)^2$  and  $(1,0,1,2^0,0)^0 \leftarrow (0,0,0,2^0,0)^0$ . This indicates either an undetected perturbation or that the effective values of  $g_{44}$  and  $g_{55}$  depend on  $v_1''$  or  $v_3''$  (or both). Recently, Rao and co-workers<sup>52</sup> have also reported effective values of  $g_{45}$  and  $r_{45}$  for (1,0,0,1,1) and  $g_{55}$  for (1,0,0,0,2) which deviate substantially from the constants obtained from states without CH stretch excitation. *Every observed stretch excited state has effective  $l$ -splitting constants which differ substantially from those for states without stretch excitation.* Although the effective  $l$ -splitting constants reported by Rao are based on only one CH stretch excited level, considered along with our observation of a large systematic effect due to CC stretching, they indicate that all three stretching vibrations have a large effect on the bending anharmonicities which produce the  $l$ -splitting (the  $l$ -splitting is identically zero if the bending vibration is harmonic). This means that the spectroscopic constants which determine the  $l$ -splittings in the stretch excited levels observed in the SEP spectrum cannot be reliably fixed at the values determined from levels without stretch excitation, and need to be separately determined.

Unfortunately, this dependence of the  $l$ -splitting constants on stretch excitation increases the number of vibra-

tional spectroscopic constants expected to be important for a physically meaningful characterization of the observed levels. Since the number of vibrational levels observed in this work is the same as the number of physically meaningful vibrational spectroscopic constants, it is not possible to accurately determine all the spectroscopic constants without introducing additional data or constraining some constants to previously reported values. SEP spectra from the perturbed  $\tilde{A} 3v_3'$  level should access  $v_5'' = 4$ , and in combination with hot band PUMPed SEP from  $K'=3$  to  $l''=4$  should allow a complete deperturbation of the SEP spectrum in this region.

Strey and Mills<sup>30</sup> encountered a difficulty in their construction of a general quadratic + cubic + quartic force field for acetylene from the available spectroscopic constants. The harmonic force field was reasonably well determined from the available spectroscopic constants for the various isotopomers. However, the values of the spectroscopic constants  $\alpha_t$  and  $(x_{tt} + 3g_{tt})$  for HCCH and DCCD, which depend only on the two cubic constants  $k_{1tt}$  and  $k_{2tt}$ , were not isotopically consistent for either bending vibration  $\nu_t$  ( $t=4$  or 5). Recent reanalysis of the bending levels of both HCCH and DCCD by Herman and co-workers<sup>33</sup> still leaves a substantial isotopic discrepancy. Since it seems plausible that the correction from zero-point to equilibrium stretching excitation (which depends on unknown quintic and higher potential terms) will change the  $g_{tt}$  constants by more than 20% in HCCH, one might hope

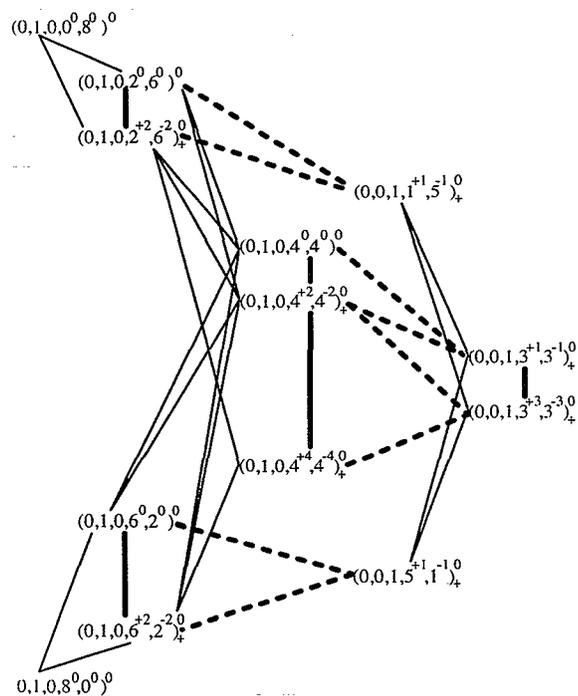


FIG. 4. Resonance diagram showing  $l=0$  levels coupled to the observed levels by Darling-Dennison resonance (solid lines), Vibrational- $l$ -resonance (bold lines) and Fermi resonance (dashed lines). The energy level pattern is roughly to scale from a complete matrix diagonalization. This figure is a fairly simple illustration of the complex mixing caused by vibrational resonances [Eqs. (6)–(9)] at modest vibrational excitation.

TABLE V. DF assignments.<sup>a</sup>

$(\nu_2, \nu_4, \nu_5)$	Term value/cm <sup>-1</sup>
(0,18,0)	11 835
(1,12,4)	12 448
(1,10,6)	12 512
(1,18,0)	13 655
(1,14,4)	13 809
(1,12,6)	13 862
(2,8,4)	11 632
(2,6,6)	11 707
(2,10,4)	12 951

<sup>a</sup>Data from Ref. 15.

that these stretching zero-point corrections will resolve the troubling isotopic discrepancy noted by Strey and Mills.

### IX. ASSIGNMENT OF THE DF SPECTRUM

All higher members of the  $\nu_2'', \nu_4''$  progressions that include the (0,1,0,6,2) level in the dispersed fluorescence spectrum can now be firmly assigned as  $(0, \nu_2'', 0, \nu_4'', 2)$  appearing through strong DD resonance with  $[0, \nu_2'', 0, (\nu_4'' + 2), 0]$ . Since a strong DD bending resonance is now firmly established, it is possible to extend the DF assignments to slightly higher energy. In the DF spectrum, the levels  $(0, \nu_2'', 0, \nu_4'', 2)$ , which lie above the levels  $[0, \nu_2'', 0, (\nu_4'' + 2), 0]$  for low  $\nu_4''$ , gradually approach the  $[0, \nu_2'', 0, (\nu_4'' + 2), 0]$  levels from above as  $\nu_4''$  is increased. The effective anharmonic constants obtained from the analysis of the DF spectra<sup>15</sup> predict that the levels  $(0, \nu_2'', 0, \nu_4'', 2)$  cross the  $[0, \nu_2'', 0, (\nu_4'' + 2), 0]$  levels from above near  $\nu_4'' = 18$ . (Pliva's anharmonic constants<sup>22</sup> predict a crossing between  $\nu_4'' = 14$  and  $\nu_4'' = 16$ .) As described by Eqs. (6) and (7), bright features with high values of  $\nu_4''$  will undergo stronger DD resonances than features with low  $\nu_4''$  and may therefore be expected to transfer intensity to higher values of  $\nu_5''$ , especially since the "unperturbed" resonating levels  $(0, \nu_2'', 0, 2n, 0)$ ,  $(0, \nu_2'', 0, (2n - 2), 2) \cdots (0, \nu_2'', 0, 0, 2n)$  are converging as  $\nu_4''$  increases. As mentioned in our prior paper,<sup>15</sup> when these groups of DD resonating levels invert, the intensities will be profoundly affected and the separate  $\nu_4'', \nu_5''$  quantum numbers will lose their meaning.

Plausible assignments of unassigned features observed in the DF spectrum below 14 000 cm<sup>-1</sup> are listed in Table V. In all cases except the  $(\nu_2'', \nu_4'')[\nu_5'' = (\nu_4'' + \nu_5'')] = (1, 18)$  feature, the assignments to the low *cis*-bend excitation levels  $(\nu_2'', \nu_4'', 0)$  and  $(\nu_2'', \nu_4'', 2)$  had already been suggested in Ref. 15, so that these assignments are just an extension of the DD resonance suggested there. Except for (0,2,0,6,6), all the assignments in Table V are fairly straightforward based on relative intensities and second differences  $\Delta_2 G(\nu)$ . Unexpected intensity patterns, such as that observed for the (0,2,0,12,0) group of features,<sup>15</sup> can also be qualitatively reproduced in our calculations. Diagonalization of the full DD/Fermi/vibrational-*l*-resonance matrix indicates substantial mixing in the normal mode basis for  $\nu_b'' \geq 12$ , with most wave functions containing less

than 35% of their nominal basis function character. Thus the  $(\nu_2'', \nu_4'', \nu_5'')$  labels are more properly regarded as energy indices. For  $\nu_b'' \geq 14$ , the calculated intensities suggest that the lowest observed level is not necessarily the lowest member of the interacting tier to which it belongs, and assignments within a tier may be meaningless (even as energy indices) for  $\nu_b'' \geq 14$ . What is important is that all of the 50 DF features below 14 000 cm<sup>-1</sup> can be securely assigned to (CC stretch, *trans*-bend) combinations and their DD resonance partners.

The extra  $l''=2$  levels observed by Chen *et al.*<sup>53</sup> are now explained by the vibrational-*l*-resonance among states with excitation of both degenerate bending vibrations reported here. All of the 11 vibrational states observed in the region between 9400 and 9700 cm<sup>-1</sup> by Abramson *et al.*<sup>18</sup> can be accounted for if it is assumed that the IVR mechanism observed here for the (0,1,0,8,0) state is exactly replicated for the (0,1,0,12,0) state, as is suggested by the analysis of the dispersed fluorescence spectrum.<sup>15</sup> Up to 18 000 cm<sup>-1</sup>, states with  $\nu_b'' \leq 18$ , which exhibit intensity/splitting patterns closely resembling those of assigned features with the same  $\nu_b''$  quantum number below 14 000 cm<sup>-1</sup>, account for the bulk of the DF intensity. Although the DF spectrum above 18 000 cm<sup>-1</sup> is qualitatively consistent with the IVR mechanism observed here and we can place upper bounds on the IVR rate from the width of the features,<sup>15</sup> we cannot rule out the appearance of new resonances above 18 000 cm<sup>-1</sup> or for states with  $\nu_b'' \geq 20$ . However, it seems *possible* that the resonances elucidated here scale with vibrational quantum numbers in the fairly simple fashion characteristic of the lowest order terms in the Hamiltonian over the entire energy range accessible by SEP.

### X. CH STRETCH FRANCK-CONDON FACTORS

Because of the change in CH bond length on  $\tilde{A} \rightarrow \tilde{X}$  emission, it was assumed by Abramson *et al.*<sup>18</sup> in their discussion of the emission spectrum of acetylene that one or two quanta of  $\nu_1''$  would have appreciable Franck-Condon intensity and should appear in the spectrum. This plausible but untested assumption that the states initially prepared by SEP have CH stretch excitation has pervaded most studies of the subsequent dynamics of the initially prepared state. Nevertheless, we have shown here that all of the 50 features observed below 14 000 cm<sup>-1</sup> in the dispersed  $\tilde{A} \rightarrow \tilde{X}$  fluorescence spectrum of acetylene can be satisfactorily accounted for as Franck-Condon bright states  $(\nu_2'', \nu_4'')$  and nominally dark states  $[\nu_2'', \nu_4'' = (\nu_4'' + \nu_5'')] appearing through DD resonance. There are no apparent progressions built on  $\nu_1''$  over the range 5 700 to 14 000 cm<sup>-1</sup> in a DF spectrum with a 100-fold range of detectable signals. Furthermore, the state (1,0,0,6,0) has not been detected in the SEP spectra near 7000 cm<sup>-1</sup> despite an estimated 500-fold range of detectable SEP signals. We present here a calculation which makes the absence of progressions built on  $\nu_1''$  plausible. The absence of CH stretch excitation in acetylene  $\tilde{A} \rightarrow \tilde{X}$  emission is entirely$

analogous to the absence of CH stretch excitation in the  $\tilde{A} \rightarrow \tilde{X}$  emission spectrum of the isoelectronic molecule HCN.<sup>54</sup>

The basic idea of our calculation is that the normal mode  $\nu_1''$  consists of a simultaneous extension of both CH bonds and a contraction of the CC bond (Ref. 5, p. 181), so that the increases in both the CH and CC bond lengths in the  $\tilde{A}$  state may cancel in the normal coordinate displacement, thus eliminating Franck–Condon excitation of  $\nu_1''$ . Neglecting the Duschinsky effect, the harmonic Franck–Condon factors can be calculated from the known harmonic frequencies  $\omega_1'', \omega_1'$ , the equilibrium geometries of the  $\tilde{A}$  and  $\tilde{X}$  states, and the normal coordinate  $q_1''$  of the ground state.<sup>55</sup> We do not expect the  $\tilde{A}$ -state *trans*-bending vibration to significantly stretch the CC or CH bonds, so that neglect of the Duschinsky effect seems reasonable for emission from  $\tilde{A}$ -state levels with no stretching excitation.<sup>56</sup> We therefore assume the CH stretch progressions in emission spectra from  $\tilde{A}$ -state levels with only *trans*-bend excitation are determined by the geometry of the  $\tilde{A}$  state and the normal modes of the  $\tilde{X}$  state, and are not very sensitive to the form of the CH stretch normal mode in the  $\tilde{A}$  state.<sup>57</sup>

The  $\tilde{X}$  state stretching normal modes are calculated from the harmonic force field of Strey and Mills<sup>30</sup> using the normal mode analysis of Shaffer and Nielsen.<sup>58</sup> Let  $\delta R$  denote the displacement of the CC bond length from equilibrium, and  $\delta r_1, \delta r_2$  denote the displacements of CH bonds 1 and 2, respectively, then the normal mode displacements are given by

$$Q_1 = -\beta(m/2)^{(1/2)}(\delta r_1 + \delta r_2) - [\alpha(M/2)^{(1/2)} + \beta(m/2)^{(1/2)}]\delta R, \quad (17)$$

$$Q_2 = -\alpha(m/2)^{(1/2)}(\delta r_1 + \delta r_2) - [\alpha(m/2)^{(1/2)} - \beta(M/2)^{(1/2)}]\delta R, \quad (18)$$

where  $\alpha$  and  $\beta$  are defined by Eq. (7) of Ref. 58,  $m$  is the atomic mass of hydrogen and  $M$  is the atomic mass of carbon. Note that we have defined the normal coordinates in terms of bond lengths rather than Cartesian coordinates defined by the Eckart condition. The reason for this is that the bending vibrations of molecules are often nearly changes in bond angles alone without any significant change in bond length. Of course, the choice of coordinates in which the normal modes are defined is immaterial in an exact calculation, but it is essential that the coordinates make the motion separable for an approximate harmonic calculation to be useful. The use of bond length and bond angle coordinates for large amplitude vibrations has been advocated by Pliva, who called them “valence force coordinates,”<sup>59</sup> and the use of similar coordinates apparently dates back at least to Mecke’s work in the 1930’s.<sup>60</sup>

For the acetylene force constants of Strey and Mills,<sup>30</sup>  $\alpha = 0.4326$  and  $\beta = -0.9016$ .<sup>61</sup> Introducing dimensionless normal coordinates<sup>62</sup>  $q_i = (2\pi c \omega_i / \hbar)^{1/2} Q_i$ , we obtain  $q_1 = 6.53(\delta r_1 + \delta r_2) - 4.24\delta R$  where the displacements are measured in Ångströms. The only completely experimen-

tally determined structure for the  $\tilde{A}$  state is the recent set of bond lengths obtained by Huet *et al.*,<sup>63</sup> who obtained  $R = 1.375$  Å,  $r = 1.097$  Å and an HCC bond angle of 122.48° from the rotational constants of HCCH and DCCD. Using the ground state bond lengths  $R = 1.208$  Å,  $r = 1.057$  Å we obtain  $q_1''|_{\tilde{A}} = -0.18(3)$  for the value of  $q_1''$  evaluated at the equilibrium geometry of the  $\tilde{A}$  state, while in dimensionless normal coordinates  $q = 1$  at the classical turning point of  $v = 0$ .<sup>64</sup> Since the form of the  $\tilde{X}$ -state normal modes is critical to the calculated displacement, we note that  $q_1''|_{\tilde{A}} = -0.18$  is also obtained from the simplified harmonic valence force field of Herzberg (Ref. 5, Table 45) dating from 1945. This result confirms our suggestion of considerable cancellation of the CH and CC contributions to the normal coordinate  $q_1''$  at the  $\tilde{A}$  state geometry for any reasonable  $\tilde{X}$  state harmonic force field.

We assume that the  $\tilde{A}$ -state normal coordinate  $q_1$  has the same form (in the “valence force coordinates”) as in the ground state in order to calculate Franck–Condon factors.<sup>65</sup> The harmonic CH stretch Franck–Condon emission factors are calculated from ratios of overlap integrals  $R(m, 0) = \int \psi_0' \psi_m'' d\tau$  following the method of Smith and Warsop:<sup>55</sup>

$$\frac{R(m+1, 0)}{R(m, 0)} = \frac{2^{1/2} \rho q}{(1+\rho)(m+1)^{1/2}} + \left(\frac{m}{m+1}\right)^{1/2} \frac{R(m-1, 0)}{R(m, 0)} \left(\frac{1-\rho}{1+\rho}\right), \quad (19)$$

where  $\rho = (\omega_1'/\omega_1'')$ ,  $q$  is the displacement in dimensionless normal coordinates, and  $R(-1, 0) \equiv 0$ . Using  $\omega_1'' = 3496$  cm<sup>-1</sup>,  $\omega_1' = 3040.6$  cm<sup>-1</sup>,<sup>21</sup> and  $q = -0.18$ , emission to  $\nu_1'' = 1$  should have  $2(\rho q)^2/(1+\rho)^2 = 0.015(2)$  of the intensity of emission to  $\nu_1'' = 0$ , and emission to  $\nu_1'' = 2$  should be down another factor of 4. An entirely similar calculation predicts maximum emission at  $\nu_2'' = 5$  in the CC stretch progression, which may be compared to the experimental maximum at  $\nu_2'' = 3$  (i.e., the calculated  $\nu_2''$  progression is longer than observed). We make no claim that this simple calculation is quantitatively accurate, but if the intensity estimate were correct, the apparent absence of CH stretch excitation in  $\tilde{A} \rightarrow \tilde{X}$  dispersed fluorescence spectra would be explained: *progressions built on  $\nu_1'' \neq 0$  would be at least a factor of 60 weaker than those built on  $\nu_1'' = 0$ .*

For the (1,0,0,6,0) level, which we did not observe in our SEP spectra, we may estimate the Franck–Condon factor relative to (0,1,0,8,0) as follows. The intensity of emission to (0,0,0,6,0) can be estimated from the DF intensities for (0,1,0,6,0), (0,2,0,6,0), (0,3,0,6,0), and (0,4,0,6,0) in Table I of Ref. 15 and the calculated Franck–Condon factors for the CC stretch. We obtain the intensity ratio  $I(0,1,0,8,0):I(0,0,0,6,0) \approx 10:1$ , so the expected intensity ratio  $I(0,1,0,8,0):I(1,0,0,6,0)$  is about 600:1. Because the calculated CC stretch Franck–Condon progression is longer than the observed progression, this calculation is likely to overestimate the intensity of

(1,0,0,6,0). Since we have estimated a 500-fold range of detectable SEP intensities in our spectra,<sup>19</sup> this calculation shows that the undetected (1,0,0,6,0) level is not expected to have enough intensity to appear in our SEP spectra.

## XI. IVR PATHWAY

We show here that the resonances discussed in Sec. VII, when combined with a resonance found in the overtone spectrum,<sup>16</sup> couple every vibrational level of *g* symmetry to an SEP bright state (0,  $v_2$ , 0,  $v_4$ , 0). In spite of this, we also demonstrate a number of restrictive rules for IVR

via these anharmonic resonances. Thus at high enough energy, *restricted* IVR should make it possible to observe *all* states of a given symmetry by SEP.

### A. Observation of the complete density of states

Consider an arbitrary state ( $v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5}$ ). We illustrate one out of many Fermi resonance paths coupling this state to the bright state [0, ( $v_1 + v_2 + v_3$ ), 0, ( $2v_1 + 2v_3 + v_4 + v_5$ ) <sup>$l_4+l_5$</sup> , 0]. First  $v_3$  2345 Fermi resonances will couple ( $v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5}$ ) to [ $v_1, (v_2 + v_3), 0, (v_3 + v_4)^{l_4+v_3}, (v_3 + v_5)^{l_5-v_3}$ ], eliminating excitation of  $v_3$ .

$$\begin{array}{ccccccc} (v_1, & v_2, & v_3, & v_4, & l_4, & v_5, & l_5) \\ +v_3 \cdot (0, & +1, & -1, & +1, & +1, & +1, & -1) \\ \hline (v_1, & v_2+v_3, & 0, & v_3+v_4, & l_4+v_3, & v_3+v_5, & l_5-v_3) \end{array}$$

( $l_4 > 0$  has been assumed. If  $l_4 < 0$ , then  $l_4 - v_3$  and  $l_5 + v_3$  should be used for  $\Sigma_g^-$  states, which cannot have  $l_4 = 0$  or  $l_5 = 0$ .) Smith and Winn<sup>16</sup> report but do not treat quantitatively (the importance of a quantitative treatment will be explained later), a  $2\Delta v_1 = -2\Delta v_2 = -\Delta v_4 = \pm 2$  Fermi resonance which can eliminate excitation of  $v_1$  by coupling to [0, ( $v_1 + v_2 + v_3$ ), 0, ( $2v_1 + v_3 + v_4$ ) <sup>$l_4+v_3$</sup> , ( $v_3 + v_5$ ) <sup>$l_5-v_3$</sup> ].

$$\begin{array}{ccccccc} (v_1, & v_2+v_3, & 0, & v_3+v_4, & l_4+v_3, & v_3+v_5, & l_5-v_3) \\ +v_1 \cdot (-1, & +1, & 0, & +2, & 0, & 0, & 0) \\ \hline (0, & v_1+v_2+v_3, & 0, & 2v_1+v_3+v_4, & l_4+v_3, & v_3+v_5, & l_5-v_3) \end{array}$$

Since we assume the level has *g* symmetry, ( $l_5 - v_3$ ) is even (because  $v_3$  and  $v_5$  are the only *u* symmetry modes) and [ $(l_5 - v_3)/2$ ] vibrational-*l*-resonances couple to a state with no *cis*-bending vibrational angular momentum, [0, ( $v_1 + v_2 + v_3$ ), 0, ( $2v_1 + v_3 + v_4$ ) <sup>$l_4+l_5$</sup> , ( $v_3 + v_5$ )<sup>0</sup>].

$$\begin{array}{ccccccc} (0, & v_1+v_2+v_3, & 0, & 2v_1+v_3+v_4, & l_4+v_3, & v_3+v_5, & l_5-v_3) \\ +[(l_5-v_3)/2] \cdot (0, & 0, & 0, & 0, & +2, & 0, & -2) \\ \hline (0, & v_1+v_2+v_3, & 0, & 2v_1+v_3+v_4, & l_4+l_5, & v_3+v_5, & 0) \end{array}$$

Finally, [ $(v_3 + v_5)/2$ ] bend DD resonances annihilate *cis*-bend excitation and couple to the SEP bright state [0, ( $v_1 + v_2 + v_3$ ), 0, ( $2v_1 + 2v_3 + v_4 + v_5$ ) <sup>$l_4+l_5$</sup> , 0<sup>0</sup>].

$$\begin{array}{ccccccc} (0, & v_1+v_2+v_3, & 0, & 2v_1+v_3+v_4, & l_4+l_5, & v_3+v_5, & 0) \\ +[(v_3+v_5)/2] \cdot (0, & 0, & 0, & +2, & 0, & -2, & 0) \\ \hline (0, & v_1+v_2+v_3, & 0, & 2v_1+2v_3+v_4+v_5, & l_4+l_5, & 0, & 0) \end{array}$$

Note that *none* of the normal mode quantum numbers is conserved. Consideration of the strong, quantitatively characterized  $\Delta v_1 = -\Delta v_3 = \pm 2$  DD resonance between the two CH stretching vibrations<sup>16,38</sup> (instead of the  $2\Delta v_1 = -2\Delta v_2 = -\Delta v_4 = \pm 2$  Fermi resonance) also leads to the latter conclusion as well, but does not yield coupling between levels with odd  $v_1$  and SEP bright states.

### B. Resonance vectors and good quantum numbers

Fried and Ezra have shown that for polynomial Hamiltonians, a resonance vector analysis<sup>66</sup> is a useful way

to identify *all* the exact quantum numbers. This approach has been applied by Kellman and co-workers<sup>67,68</sup> to the resonances observed in the overtone spectrum of acetylene. However, their analysis did not include the vibrational angular momenta, the Darling–Dennison bend resonance reported here, or the vibrational-*l*-resonance, all of which play an important role in acetylene  $\tilde{A} \rightarrow \tilde{X}$  emission spectra.

In a resonance vector analysis, the set of quantum numbers is written as a vector ( $v_1, v_2, v_3, v_4, l_4, v_5, l_5$ ), as are the resonances. The vectors for the quantitatively treated resonances are

vibrational- <i>l</i> -resonance	(0,0,0,2,0,-2),	
DD bend resonance	(0,0,0,2,0,-2,0)	
	(0,0,0,2,2,-2,-2)	
	(0,0,0,2,-2,-2,2),	(20)
2345 Fermi resonance	(0,1,-1,1,-1,1,1)	
	(0,1,-1,1,1,1,-1),	
DD stretch resonance	(2,0,-2,0,0,0,0).	

Note that the third, fourth and sixth resonance vectors are linear combinations of the remaining four, which are linearly independent. Thus three orthogonal vectors in the seven-dimensional space of quantum numbers form a basis for the space orthogonal to the four-dimensional space spanned by the resonance vectors, and represent good quantum numbers for the short time dynamics. By inspection, the vectors (1,1,1,0,0,0) and (0,0,0,0,1,0,1) are orthogonal to each other and all of the resonance vectors. Ezra's modified Gram-Schmidt orthogonalization procedure<sup>66</sup> shows that the vector (2,-4,2,3,0,3,0) is orthogonal to all of the above resonance vectors.

These three vectors thus represent good quantum numbers for the short time dynamics, when other resonances can be neglected. The vector (1,1,1,0,0,0,0) represents the total stretching quantum number  $n''_s = (v''_1 + v''_2 + v''_3)$ . Similarly, (0,0,0,0,1,0,1) represents the total vibrational angular momentum quantum number  $l''$ . The significance of the third good quantum number is not immediately obvious, but Kellman<sup>67</sup> has pointed out that the linear combination  $(2,-4,2,3,0,3,0) + 13(1,1,1,0,0,0,0) = 3(5,3,5,1,0,1,0)$  has a simple interpretation as a quantum number representing the "resonance condition" that strongly interacting levels have approximately the same energy,  $n''_{\text{res}} = (5v''_1 + 3v''_2 + 5v''_3 + v''_4 + v''_5)$ .

### C. IVR restrictions

At high energy, these intramolecular vibrational relaxation pathways can transfer most of the vibrational energy out of the Franck-Condon bright vibrational modes  $v''_2$  and  $v''_4$  on a timescale of a few hundred femtoseconds. However, the strongest resonances obey some interesting rules. These rules are *local* restrictions on the short time dynamics which are not necessarily obvious from the approximate quantum numbers representing *global* restrictions on the short time dynamics. For the purposes of illustrating these rules, we use  $(V''_2, V''_4)$  to denote the vibrational quantum numbers of the initial zero-order Franck-Condon bright state, and the standard normal mode quantum numbers for the eigenstates coupled to a single  $(V''_2, V''_4)$  bright state by the strong resonances listed above [Eq. (20)]. These local, short time IVR restrictions follow: (i) A normal mode state coupled to one bright state  $(V''_2, V''_4)$  is not coupled to any other since  $V''_2 = n''_s$  and  $V''_4 = n''_{\text{res}} - 3n''_s$  are conserved. (ii) None of the resonances can increase  $v''_b = (v''_4 + v''_5)$  so that it becomes greater than  $V''_4$ . (iii) Since every resonance which destroys two bending quanta also destroys one CC stretching quantum, the number of destroyed bending quanta

$(V''_4 - v''_b)$  cannot be greater than  $2V''_2$ . A corollary of rule (iii) is that *pure trans*-bending overtones are decoupled from the stretching states for short times. (iv) Combining rules (ii) and (iii), the total bending excitation is bounded both above and below  $V''_4 \geq v''_b \geq (V''_4 - 2V''_2)$ . These are clearly severe restrictions on the accessible range of quantum numbers (phase space) that the initial bright state explores during the first few hundred femtoseconds. *In particular, each vibrational state is coupled to only one bright state by IVR on this time scale.* The range of quantum numbers accessed by the short time dynamics varies drastically with  $V''_2$  and  $V''_4$ . For instance, states with  $V''_4 = 2V''_2 = 4n$  (where  $n$  is an integer) can couple to the states  $v''_3 = 2n$  which appear as hot bands from  $v_3$  in the overtone spectrum! This is the first contact between acetylene states observed by SEP and states observed by CH overtone spectra. Excitation of the CC stretch promotes bend-stretch coupling for the highly excited bending states discussed here. All of the bend-stretch coupling in the overtone spectrum also involves the CC stretch.<sup>16</sup> Evidently, CC stretch excitation is almost universally required for strong bend-stretch coupling, and acts almost as an on-off switch for IVR in acetylene.

## XII. DISCUSSION

Kellman has noted the surprising fact that all but one of the 12 resonances identified, but not quantitatively treated, by Smith and Winn<sup>16</sup> in the overtone spectrum above  $10\,000\text{ cm}^{-1}$  preserve both approximate vibrational quantum numbers  $n''_s$  and  $n''_{\text{res}}$  (by definition, "vibrational" resonances cannot alter the "rotational" quantum number  $l''$ ).<sup>32</sup> Furthermore, Kellman points out that there is reason to question the one resonance which does not preserve these quantum numbers. This remarkable observation might be most simply explained by noting that within the perturbation theory or contact transformation framework traditional in molecular spectroscopy, *sums and differences of resonance vectors are also resonance vectors* in higher orders of the theory. (In contrast to approximate quantum numbers, noninteger multiples of resonance vectors are not necessarily resonance vectors.) It is possible that many resonances are caused by a much smaller number of coupling terms in the potential energy.

Physically, the sum (difference) of two resonance vectors corresponds to an indirect coupling between two states through an intermediate level. Such couplings can often be quantitatively treated using standard Van Vleck (contact) transformations. Indirect couplings which correspond to the sum of two resonance vectors have a "normal" dependence on the vibrational quantum numbers [e.g., if  $v_i$  increases by  $n$  units, the off-diagonal matrix element is proportional to  $\sqrt{(v_i+1)(v_i+2)\cdots(v_i+n)}$ ], but the apparent resonance constants can be calculated from the direct coupling constants and the position of the intermediate level. Indirect resonances corresponding to the difference of two resonance vectors have a higher order dependence on the vibrational quantum numbers than one would naively expect [possibly including a dependence on un-

changed vibrational quantum numbers, e.g., Eq. (13)], but the resonance constants can again be calculated.

Thus the simplest explanation for the wealth of resonances in the overtone spectrum at high energy is that most of the resonances are indirect. With the exception of the  $4\Delta v_1 = 2\Delta v_3 = -\Delta v_2 = -2\Delta v_4 = \pm 4$  resonance, questioned by Kellman, all of the resonance vectors for the resonances in Table V of the paper by Smith and Winn<sup>16</sup> may be written as sums and differences of the resonance vectors in Eq. (20) and the resonance vector  $(-1, 1, 0, 2, 0, 0, 0)$  of the  $2\Delta v_1 = -2\Delta v_2 = -\Delta v_4 = \pm 2$  Fermi resonance. Thus only one additional direct resonance due to a coupling term in the Hamiltonian is required to explain the resonances found by Smith and Winn (there may, of course, be more than one). Since the levels involved in the resonances listed in Table V of Ref. 16 have high vibrational quantum numbers, it is also possible that  $(-1, 1, 0, 2, 0, 0, 0)$  is actually an indirect “difference” resonance and one of the other resonances is in fact direct. Calculations by Bramley *et al.*<sup>45</sup> indicate a direct resonance between  $\nu_1'$  and  $(\nu_2 + 2\nu_5^0)^0$ , which would allow indirect  $2\Delta v_1 = -2\Delta v_2 = -\Delta v_4 = \pm 2$  resonances through DD bend resonance [Eq. (6)]. Recently, Lehmann<sup>69</sup> has shown that indirect resonances in HCCF can be quantitatively calculated from the direct coupling of two states to a common intermediate, and such analysis seems desirable for the overtone spectrum of acetylene.

By analogy to classical mechanics, we believe the approximate quantum number  $n''_{\text{res}}$ , which at first seems trivial, is especially significant for IVR. The approximate quantum number  $n''_{\text{res}}$  may be viewed as a reflection of the fact that for all the strong resonances discussed above, the five normal mode frequencies are in the ratio 5:3:5:1:1. Classically, when the oscillation frequency depends on the amplitude (nonlinear oscillations) it is possible to have resonances with *different frequency ratios* between *the same two modes* and the overlapping of resonances with different frequency ratios is a frequently applied criterion for chaos (Chirikov’s overlapping resonances).<sup>70,71</sup> Classically, sequential resonances with the *same frequency ratios between different modes* lead to much slower exchange of energy between modes (Arnold diffusion).<sup>72</sup> By analogy,  $n''_{\text{res}}$  may represent a particularly significant impediment to IVR, since it not only limits the accessible phase space but also reduces the rate of phase space exploration (see Ref. 28, pp. 267–269). Since the vibrational frequencies are known to change significantly for the vinylidene isomer, the onset of acetylene–vinylidene isomerization<sup>73</sup> at  $E_{\text{VIB}} \approx 16\,000\text{ cm}^{-1}$  may increase the IVR rate by causing resonances with different frequency ratios to appear.

It is not clear whether the splitting of DF features in the SEP spectrum reflects intrinsically complex vibrational dynamics of the  $\tilde{X}$  state or simply the difference between the Franck–Condon bright normal modes and the “natural dynamical variables” (i.e., angles conjugate to conserved actions) of the highly vibrationally excited ground state. The intensity of a transition to a given vibrational level in the SEP experiment is approximately determined by its Franck–Condon bright normal mode character. If the

ground state dynamics is more appropriately described by some other simple model, the quantum numbers of that model may be perfectly good, but the intensity in the SEP experiment will still be distributed according to the normal mode character.

The vibron model of Iachello and co-workers treats the resonances between the bending vibrations with a remarkably small number of parameters,<sup>74</sup> and may be an important step in simplifying the physical picture of interactions between the bending vibrations, which are certainly complex in the normal mode basis. Although the observed small  $l''=0, 2$  splittings for the levels in vibrational- $l$ -resonance are obtained from calculations using the matrices in Sec. VII, we did not intuitively expect them from the form of the matrices for  $l''=0$  and 2 in Sec. VII. The “obvious” explanation as small “local rotor” splittings in a nearly harmonic “local bender” picture appears to conflict with the available potential surface.<sup>75</sup>

The elucidation of the next steps in the vibrational energy flow which follow the strong resonances discussed above is obviously an important task. The observation that each normal mode state is only coupled to one Franck–Condon bright state would have a very specific spectroscopic signature if it were to hold for the long time dynamics: the relative intensities of the SEP peaks under an isolated Franck–Condon bright state would not depend on the vibrational level of the  $\tilde{A}$  state used as the SEP intermediate.<sup>76</sup> SEP spectra of a single Franck–Condon bright state, recorded from two different  $\tilde{A}$ -state vibrational levels, could probe the extent to which this rule that vibrational energy does not flow between zero-order bright states breaks down at long times. If two such SEP spectra recorded from different  $\tilde{A}$ -state vibrational levels exhibited nearly identical relative intensities for all the transitions under a feature in both spectra, it would prove that the vibrational motion is largely localized in a small region of phase space, even for the long time dynamics.

### XIII. CONCLUSION

The resonances found here play an important role in redistributing the initial CC stretch/*trans*-bend excitation prepared by  $\tilde{A} \rightarrow \tilde{X}$  emission over the other vibrational degrees of freedom. It is clearly important to obtain precise values of the anharmonic coupling constants which appear in the off-diagonal matrix elements. This would enable simple scaling predictions of the energy flow rates and pathways in the spectrum at higher energy and would be useful in determining the potential surface.<sup>77</sup> A failure of simple scaling would be symptomatic of a change in the dynamics (e.g., a new IVR pathway, the appearance of local modes). Two efforts along this direction are proposed. The observation of  $l''=4$  levels is possible using the securely assigned two quanta hot band  $\tilde{A}(0, 0, 2, 0, 0, 0)^3 \leftarrow \tilde{X}(0, 0, 0, 2^2, 0)^2$  PUMP transition, and should overdetermine the data set for a severe quantitative test of the DD/Fermi/vibrational- $l$ -resonance model proposed here. A second possible experiment uses the perturbed  $\tilde{A}(0, 0, 3, 0, 0, 0)^1$  level<sup>78</sup> as the SEP intermediate. All of the presently proposed assignments for the perturber<sup>79</sup> involve

excitation of two or four quanta in the  $\tilde{A}$ -state normal modes  $\nu'_4$  and  $\nu'_6$ , which correlate to *cis*-bending in the  $\tilde{X}$  state. Since the  $\tilde{A} \leftrightarrow \tilde{X}$  transition is essentially Franck-Condon vertical with respect to the *cis*-bend, states with either two or four quanta of *cis*-bend will be Franck-Condon bright from the perturber, providing valuable information about both the  $\tilde{A}$ -state perturber and the  $\tilde{X}$ -state levels with four quanta of *cis*-bending excitation. If the  $\tilde{A}(0,0,3,0,0,0)^1$  perturbation involves a secondary *a*-axis or *b*-axis Coriolis coupling (as suggested in Refs. 78 and 79) which can couple  $B_g$  symmetry vibrational states to the  $A_g$  vibrational symmetry  $\tilde{A}(0,0,3,0,0,0)^1$  level, the Coriolis perturber would allow access to  $\Sigma_g^-$  symmetry vibrational levels of the ground electronic state, which correlate to  $B_g$  symmetry at the *trans*-bent geometry.

The absence of significant CH stretch excitation on  $\tilde{A} \rightarrow \tilde{X}$  emission completely alters the previously accepted picture of vibrational energy flow in highly excited acetylene.<sup>20</sup> The dominant energy flow path requires the DD resonance to transfer excitation from the *trans*-bend to the *cis*-bend before coupling to the other vibrational modes sets in, but this flow to the other modes apparently requires CC stretch excitation. On the short time scales dominated by the resonances studied here, the vibrational energy flow seems to obey some very restrictive rules, and at least three approximate constants of the motion exist for the short-time dynamics. The picture presented here provides a qualitatively coherent picture of the short time vibrational dynamics in acetylene over the entire energy range sampled by the dispersed fluorescence spectra. A quantitative test of the simple scaling of resonance interactions described here will involve fitting the anharmonic resonances over the entire DF spectrum, and may reveal some surprises, since the vibrational quantum numbers are much higher and weak resonances which are not apparent here may cause noticeable effects.

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## APPENDIX

This Appendix outlines the calculation of the spectroscopic constant  $s_{45}$  which appears in the off-diagonal Darling-Dennison resonance matrix elements [Eq. (6)] from spectroscopic constants reported in the literature. This calculation is only approximate because the potential is expressed in dimensionless normal coordinates (defined in terms of rectilinear Cartesian coordinates for computational expediency) and truncated above quartic terms. The stretching normal modes have been calculated from the geometry and harmonic force field of Strey and Mills,<sup>30</sup> the bending harmonic frequencies have been fit to the experimental values reported by Strey and Mills using the recti-

linear normal mode analysis of Shaffer and Nielsen,<sup>58</sup> and experimental spectroscopic constants  $x_{it'}$ ,  $g_{it'}$ ,  $\alpha_t$ , and  $r_{45}$  were taken from Strey and Mills. The vibrational corrections to the rotational constants for the two bending vibrations are given by

$$\alpha_4 = -B_e [4\pi c (\hbar/I_e)^{1/2} (\delta \lambda_2^{-3/4} k_{244} - \gamma \lambda_1^{-3/4} k_{144}) + (B_e/\omega_4) \{ \gamma^2 [(3\lambda_4 + \lambda_2)/(\lambda_4 - \lambda_2)] + \delta^2 [(3\lambda_4 + \lambda_1)/(\lambda_4 - \lambda_1)] \}], \quad (\text{A1})$$

$$\alpha_5 = -B_e [4\pi c (\hbar/I_e)^{1/2} (\delta \lambda_2^{-3/4} k_{255} - \gamma \lambda_1^{-3/4} k_{155}) + (B_e/\omega_5) \{ (3\lambda_5 + \lambda_3)/(\lambda_5 - \lambda_3) \}], \quad (\text{A2})$$

where  $\gamma$  and  $\delta$  are defined by Eq. (17) of Ref. 58,  $\lambda_i = (2\pi c \omega_i)^2$ , and  $I_e$  and  $B_e$  are the equilibrium moment of inertia and rotational constant, respectively. Equation (A1) (Eq. (A2)) yields a linear function for  $k_{144}$  ( $k_{155}$ ) in terms of  $k_{244}$  ( $k_{255}$ ) and the experimentally known value of  $\alpha_4$  ( $\alpha_5$ ). The bending anharmonic and *l*-splitting constants are given by

$$x_{it} = (1/4) \left[ 6k_{itit} - \sum_{i=1}^2 k_{itit}^2 (8\omega_i^2 - 3\omega_j^2) / [\omega_i (4\omega_i^2 - \omega_j^2)] \right], \quad (\text{A3})$$

$$g_{it} = - (1/4) \left[ 2k_{itit} + \sum_{i=1}^2 k_{itit}^2 \omega_i / (4\omega_i^2 - \omega_j^2) \right]. \quad (\text{A4})$$

Since each sum  $x_{it} + 3g_{it}$  depends only on  $(k_{1it})^2$  and  $(k_{2it})^2$ , and  $k_{1it}$  can be expressed as a linear function of  $k_{2it}$  and  $\alpha_t$ , we obtain a quadratic equation for  $k_{1it}$  in terms of  $\alpha_t$  and  $x_{it} + 3g_{it}$ . Since there are two solutions for each quadratic equation, we choose the solution which predicts the  $\alpha_t$  for DCCD most accurately.<sup>80</sup> We can obtain  $k_{4455}$  from

$$x_{45} = k_{4455} - \sum_{i=1}^2 k_{i44} k_{i55} / \omega_i + (1/2) r_{45}, \quad (\text{A5})$$

allowing us to calculate the off-diagonal DD resonance constant,

$$s_{45} = k_{4455} + (1/2) \sum_{i=1}^2 k_{i44} k_{i55} \omega_i \{ [1/(4\omega_4^2 - \omega_i^2)] + [1/(4\omega_5^2 - \omega_i^2)] \} + (1/2) r_{45} + g_{45}. \quad (\text{A6})$$

The final result is  $s_{45} = -9.3 \text{ cm}^{-1}$ , in good agreement with the values obtained from the approximate isotopic rule and deduced from the DF intensities (see Ref. 15). A rough idea of the probable error can be obtained by comparing the calculated value of  $s_{45} = -5.3 \text{ cm}^{-1}$  for DCCD with the experimental result<sup>33</sup>  $|s_{45}| = 7.96 \text{ cm}^{-1}$ .

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- <sup>33</sup>(a) T. R. Huet, M. Herman, and J. W. C. Johns, *J. Chem. Phys.* **94**, 3409 (1991); (b) M. Herman, T. R. Huet, Y. Kabbadj, and J. Vander Auwera, *Mol. Phys.* **72**, 75 (1991); (c) Y. Kabbadj, M. Herman, G. Di Lonardo, L. Fusina, and J. W. C. Johns, *J. Mol. Spectrosc.* **150**, 535 (1991).
- <sup>34</sup>W. J. Lafferty and R. J. Thibault, *J. Mol. Spectrosc.* **14**, 79 (1964).
- <sup>35</sup>W. J. Lafferty and A. S. Pine, *J. Mol. Spectrosc.* **141**, 223 (1990).
- <sup>36</sup>A.-M. Tolonen and S. Alanko, *Mol. Phys.* **75**, 1155 (1992). The 2345 Fermi resonance matrix element  $W_0$  defined by Tolonen and Alanko differs from that used here and in references 16, 34, 35, and 37-41 ( $K_{2345} = -2\sqrt{2}W_0$ ), but the transformation to the parity basis is correct.
- <sup>37</sup>R. D'Cunha, Y. A. Sarma, V. A. Job, G. Guelachvili, and K. N. Rao, *J. Mol. Spectrosc.* **157**, 358 (1993).
- <sup>38</sup>J. Vander Auwera, D. Hurtmans, M. Carleer, and M. Herman, *J. Mol. Spectrosc.* **157**, 337 (1993). Note that the discrepant  $|K_{2345}|$  value quoted for  $3v_3'$  in this paper has been corrected (Ref. 41).
- <sup>39</sup>H. Finsterhölzl, H. W. Schrötter, and G. Strey, *J. Raman Spectrosc.* **11**, 375 (1981). This paper contains a consistent treatment of the Fermi resonances in the overtone spectrum, but two slight errors should be corrected: (i) the off-diagonal element in the first matrix in column two on p. 381 should be  $(1/2\sqrt{2})K_{2345}$  [instead of  $(1/\sqrt{2})K_{2345}$ , which is a typographical error only and did not affect the analysis]; (ii) justifiably, there is no discussion of the sign of  $K_{2345}$  specified in Table I, as it cannot be determined from the available data in Refs. 34-41 [a cofactor expansion of all matrices used shows that the secular determinants depend only on  $(K_{2345})^2$  and thus only the absolute value  $|K_{2345}|$  can be determined from the vibrational term values]. The  $2v_3'$  perturbation discussed by Finsterhölzl *et al.* has since been reassigned (see Ref. 16).
- <sup>40</sup>J. F. Scott and K. N. Rao, *J. Mol. Spectrosc.* **20**, 438 (1966).
- <sup>41</sup>M. Herman, T. R. Huet, and M. Vervloet, *Mol. Phys.* **66**, 333 (1989); M. Herman and T. R. Huet, *ibid.* **70**, 545 (C) (1990). Possible errors in the simple intensity model used to calculate  $|K_{2345}|$  in this paper are discussed in Ref. 16. Because these errors are less important for stronger transitions, the estimate of  $|K_{1133}|$  in the Corrigendum is probably as reliable as the estimate based on the  $x$ - $K$  relations in Table I.
- <sup>42</sup>It follows that the state observed at  $20\,332\text{ cm}^{-1}$  in the overtone spectrum [Ref. 16(b)] cannot be  $(0,7,0,11^1,1^{-1})_0^-$ , since this state cannot steal intensity from  $(3,2,3,0,0)$  through coupling to  $(0,7,0,11^1,1^{-1})_0^+$ .
- <sup>43</sup>C. P. Rinsland, A. Baldacci, and K. Narahari Rao, *Astrophysical Journal Supplement Series* **49**, 487 (1982).
- <sup>44</sup>The negative distortion constants are very likely a result of rotational- $l$ -resonance (see Sec. V) between the observed  $l''=0$  levels and unobserved  $l''=2$   $e$  levels. The  $l''=2$  levels are unperturbed by Fermi resonance and expected to lie about  $1.5\text{ cm}^{-1}$  below the zero-order energies of the  $l''=0$  levels for doubly excited *trans*-bend levels involved in 1234 resonance. Whichever  $l''=0$  level ends up above the unobserved  $l''=2$  level will have some doubly excited *trans*-bend  $l''=0$  character and will be pushed up at high  $J$  by rotational- $l$ -resonance with the unobserved  $l''=2$  level, which is otherwise unperturbed by the Fermi resonance. For the 2345 Fermi assignment, the  $l''=2$  levels are expected to lie about  $16\text{ cm}^{-1}$  above the  $l''=0$  levels, and the perturbation shifts are not large enough to reverse this energetic ordering. Thus an explanation for the observed negative centrifugal distortion constants would require invoking yet another perturbation for the 2345 Fermi perturbation assignment.
- <sup>45</sup>M. J. Bramley, S. Carter, N. C. Handy, and I. M. Mills, *J. Mol. Spectrosc.* **157**, 301 (1993).
- <sup>46</sup>D. M. Jonas, S. A. B. Solina, B. Rajaram, R. J. Silbey, and R. W. Field (in preparation).
- <sup>47</sup>S. Gerstenkorn and P. Luc, *Atlas du Spectre de la Molecule de l'Iode entre 14,800-20,000 cm<sup>-1</sup>* (Editions du C.N.R.S., 15 quai Anatole-France, 75700 Paris); S. Gerstenkorn and P. Luc, *Rev. Phys. Appl.* **14**, 791 (1979).
- <sup>48</sup> $A$ -state term values ( $\pm 0.007\text{ cm}^{-1}$  accuracy) were obtained by simultaneous  $^{130}\text{Te}_2$  calibration of the fundamental of the doubled dye laser used to record acetylene fluorescence excitation spectra. S. A. B. Solina, J. P. O'Brien, S. J. Cohen, and R. W. Field (in preparation).
- <sup>49</sup>Only in the case of  $v_4' = 1$  or  $v_5' = 1$  is the splitting between  $l''=1$   $e$  and  $f$  parity components due to rotational- $l$ -doubling sufficiently small for  $J''=2$   $l''=1$   $e$  and  $f$  parity levels to be degenerate within the  $0.02\text{ cm}^{-1}$  experimental precision.
- <sup>50</sup> $l=2$   $f$  components can be perturbed by  $\Sigma^- l=0$  levels, but  $\Sigma^- l=0$  levels are not expected to be nearly degenerate with  $l=2$  levels because

- of the vibrational- $l$ -doubling of  $\Sigma^- l=0$  levels. Above  $J=4$ , both components of an  $l=2$  level can also be perturbed by the components of  $l=4$  levels, which both lie further away than the  $l=0$  level [see Eq. (3)] and are connected by smaller matrix elements [see Eq. (13)].
- <sup>51</sup> A. Baldacci, S. Ghersetti, and K. N. Rao, *J. Mol. Spectrosc.* **68**, 183 (1977).
- <sup>52</sup> R. D'Cunha, Y. A. Sarma, G. Guelachvili, R. Farreno, Q. Kou, V. M. Devi, D. C. Benner, and K. N. Rao, *J. Mol. Spectrosc.* **148**, 213 (1991).
- <sup>53</sup> Y. Chen, S. Halle, D. M. Jonas, J. L. Kinsey, and R. W. Field, *J. Opt. Soc. Am. B* **7**, 1805 (1990).
- <sup>54</sup> D. M. Jonas, X. Yang, and A. M. Wodtke, *J. Chem. Phys.* **97**, 2284 (1992).
- <sup>55</sup> W. L. Smith and P. A. Warsop, *Trans. Faraday Soc.* **64**, 1165 (1968).
- <sup>56</sup> Since the  $A$ -state symmetric stretching normal modes are expected to stretch both the CC and CH bonds, it would perhaps be naive to expect neglect of the Duschinsky effect for emission from  $A$ -state CC stretch excited levels to be a reasonable approximation.
- <sup>57</sup> Note that the form of the  $A$  state normal modes is crucial for  $v_1^- \leftarrow v_1'' = 0$  Franck-Condon factors in the absorption spectrum.
- <sup>58</sup> W. H. Shaffer and A. H. Nielsen, *J. Chem. Phys.* **9**, 847 (1941). Note that the numbering of the normal vibrations in Shaffer and Nielsen's 1941 paper,  $\omega_1$  is the "CC" stretch,  $\omega_2$  is the "CH" stretch,  $\omega_4$  is the *cis*-bend, and  $\omega_5$  is the *trans*-bend) differs from the standard numbering established in Herzberg's 1945 monograph. Three typographical errors in this paper are corrected here because they are relevant for the discussion in this paper: The primes on the displacement coordinates on the left-hand side of Eq. (1) were omitted; In Eq. (2),  $\mu_2 = 2mM(R+r)^2/[MR^2+m(R+2r)^2]$ ; In Eq. (22), the formula for  $x_{kk}$  ( $k=4,5$ ) has the subscripts  $i$  and  $k$  interchanged on all the harmonic frequencies inside the summation, the correct formula is given here in Eq. (A3). Certain terms in the potential energy which were omitted in Shaffer and Nielsen's paper are discussed in F. L. Keller, A. H. Nielsen, and W. H. Shaffer, *J. Chem. Phys.* **25**, 175 (1956), but the phase convention used is not explicitly stated. The discussion presented by Keller *et al.* is correct if the phase angle ( $\phi_5 - \phi_4$ ) is restricted to the range  $[0, \pi]$ .
- <sup>59</sup> J. Plíva, *Coll. Czech. Chem. Commun.* **23**, 777 (1958).
- <sup>60</sup> R. Mecke, *Z. Elektrochem.* **36**, 589 (1930).
- <sup>61</sup> The harmonic force constants of Shaffer and Nielsen (Ref. 58) ( $k_1, k_{12}, k_2$ ), expressed in terms of the harmonic force constants of Strey and Mills (Ref. 30) ( $f_{rr}, f_{r'r'}, f_{RR},$  and  $f_{rR}$ ), are  $k_1 = 2(f_{RR} + f_{r'r'}/2 + f_{r'r'}/2 - 2f_{rR})$ ;  $k_{12} = (f_{rr} + f_{r'r'} - 2f_{rR})$ ; and  $k_2 = (f_{rr} + f_{r'r'})$ . (We thank Dr. Joseph Bentley for pointing out that the negative sign for the  $f_{r'r'}$  terms found in D. M. Jonas, Ph.D. thesis, MIT, 1992 is incorrect.)
- <sup>62</sup> H. H. Nielsen, *Rev. Mod. Phys.* **23**, 90 (1951).
- <sup>63</sup> T. R. Huet, M. Godefroid, and M. Herman, *J. Mol. Spectrosc.* **144**, 32 (1990).
- <sup>64</sup> If the normal coordinate  $q_1$  is defined in terms of Cartesian displacements along the Eckart  $z$  axis, a large negative displacement ( $q_1^0 | \lambda \approx -3$ ) would be obtained, despite the fact that the CH bond has been stretched, because the projection of the CH bond on the Eckart  $z$  axis is reduced at the bent geometry.
- <sup>65</sup> Although the Duschinsky effect could mix the CH stretching and the *trans*-bending vibrations in the  $A$  state, such mixing should be weak because of the large frequency difference, and the neglect of the Duschinsky effect seems reasonable.
- <sup>66</sup> L. E. Fried and G. S. Ezra, *J. Chem. Phys.* **86**, 6270 (1987).
- <sup>67</sup> M. E. Kellman, *J. Chem. Phys.* **93**, 6630 (1990).
- <sup>68</sup> M. E. Kellman and G. Chen, *J. Chem. Phys.* **95**, 8671 (1991).
- <sup>69</sup> K. K. Lehmann, *J. Chem. Phys.* **96**, 1636 (1992).
- <sup>70</sup> M. C. Gutzwiller, *Chaos in Classical and Quantum Mechanics*, (Springer, New York, 1990), Chap. 9.
- <sup>71</sup> A. J. Lichtenberg and M. A. Leiberman, *Regular and Stochastic Motion* (Springer, New York, 1983), Chap. 4.
- <sup>72</sup> V. I. Arnold, *Geometrical Methods in the Theory of Ordinary Differential Equations* (Springer, New York, 1983), Sec. 19.
- <sup>73</sup> Y. Chen, D. M. Jonas, J. L. Kinsey, and R. W. Field, *J. Chem. Phys.* **91**, 3976 (1989).
- <sup>74</sup> F. Iachello, S. Oss, and R. Lemus, *J. Mol. Spectrosc.* **149**, 132 (1991).
- <sup>75</sup> K. K. Lehmann, *J. Chem. Phys.* **96**, 8117 (1992).
- <sup>76</sup> Perturbed SEP intermediate levels will give access to bright states other than  $mv_2'' + nv_4''$ . These unusual bright states may be coupled to each other by the fastest resonances.
- <sup>77</sup> One very interesting aspect of the resonances discussed here is that they convert the initial CC stretch/*trans*-bend excitation into *cis/trans* combinations, which effectively bend one hydrogen at a time, and symmetric/antisymmetric CH stretching combinations, which stretch one CH bond. This suggests that the resonances promote acetylene-vinylidene isomerization, since the vinylidene structure is attained by bending and stretching one CH bond. An intriguing shift of viewpoint suggests that the vinylidene portion of the potential causes the resonances observed here in the same sense that dissociation typically "causes" negative anharmonicities: both the stretching and the bending frequencies associated with a given bond usually drop with increasing vibrational amplitude. A determination of the sign of  $K_{2345}$  from SEP intensities should be possible since the signs of some of the other off-diagonal elements are known from work in the infrared (Refs. 22,23). The sign of  $K_{2345}$  would thus indicate whether the resonances found here are possibly related to acetylene-vinylidene isomerization by providing the sign and magnitude of the  $k_{2345}$  term in the potential.
- <sup>78</sup> G. J. Scherer, Y. Chen, R. L. Redington, J. L. Kinsey, and R. W. Field, *J. Chem. Phys.* **85**, 6315 (1986).
- <sup>79</sup> A. L. Utz, J. D. Tobiasson, E. Carrasquillo M., L. J. Sanders, and F. F. Crim, *J. Chem. Phys.* **98**, 2742 (1993).
- <sup>80</sup> Note that since the potential is expressed in dimensionless normal coordinates for HCCH, the constants  $k$  for HCCH need to be transformed to "real" coordinates (e.g., bond displacements) and then to dimensionless normal coordinates for DCCD to obtain the constants  $k$  for DCCD. We obtain  $\alpha_4^{d_2} = -0.00203 \text{ cm}^{-1}$  and  $\alpha_5^{d_2} = -0.00180 \text{ cm}^{-1}$ , compared to the experimental values (Ref. 30)  $-0.00201$  and  $-0.00205 \text{ cm}^{-1}$ , respectively. For  $\text{H}^{13}\text{C}^{13}\text{CH}$ , we obtain  $\alpha_4^{13c_2} = -0.00096 \text{ cm}^{-1}$  and  $\alpha_5^{13c_2} = -0.00185 \text{ cm}^{-1}$ , compared to the experimental values (Ref. 30)  $-0.00096$  and  $-0.00171 \text{ cm}^{-1}$ , respectively. Bearing in mind that the  $\alpha_i^{b_2}$  are reproduced exactly, the calculated  $\alpha_i$  constants are better than we have any right to expect [they are closer to experiment than both Strey and Mills' calculation (Ref. 30) and the recent calculations by Bramley *et al.* (Ref. 45)]. Based on the discussion in Sec. VIII, this *might* be attributed to contamination of the  $g_u^0$  constants (but not the  $\alpha_i$  constants) by quintic and higher terms in the potential, but it could be simply a fortuitous cancellation of errors in rectilinear normal coordinates.