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Intramolecular vibrational relaxation and forbidden transitions in the SEP spectrum of acetylene

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The densities of vibrational states determined from stimulated emission pumping (SEP) spectra of acetylene^{1,2} over the range $E_{\text{VIB}} = 15\,000\text{--}27\,900\text{ cm}^{-1}$ have always significantly exceeded the best calculations of the type used in statistical unimolecular reaction rate theory.³ Since the SEP measurements of the acetylene density of states are direct tests of these calculations at chemically significant energies, the discrepancy is troubling. This communication reports observations of (i) a sequence of vibrational resonances responsible for the initial stages of intramolecular vibrational relaxation (IVR); (ii) unexpected forbidden rotational transitions in high resolution SEP spectra of acetylene \tilde{X} -state vibrational levels near $E_{\text{VIB}} = 7000\text{ cm}^{-1}$; (iii) analysis of rotational line intensities and a comparison to the dispersed fluorescence (DF) spectrum which shows that the sensitivity of SEP is much greater than suggested by the range of weakest to strongest detectable fluorescence dips. Recognition of this sensitivity may be valuable for the interpretation of SEP spectra of other molecules. For acetylene, rapid IVR by specific, fully assigned resonances and the appreciable intensity of nominally forbidden rotational transitions explain the high density of observed states and several other previously reported anomalies.

The $\tilde{A}\text{--}\tilde{X}$ transition moment of acetylene is perpendicular to the plane of the *trans*-bent \tilde{A} state and is expected to imply $\Delta K \equiv K' - \ell' = \pm 1$ rotational selection rules.⁴ 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, $\tilde{A}\text{--}\tilde{X}$ emission spectra contain long progressions in combinations of the "CC" stretch, ν_2' , and the *trans*-bend, ν_4' , as expected from the Franck-Condon principle. Since there is a slight decrease in CH bond length on $\tilde{A}\text{--}\tilde{X}$ emission but no distortion or significant frequency change for ν_3' and ν_5' , two additional progressions had been tentatively assigned as built on symmetric "CH" stretch, ν_1' excitation.²

Recently, we argued that the two additional progressions observed in low resolution (30 cm^{-1}) $\tilde{A}\text{--}\tilde{X}$ DF spectra of acetylene could be better explained by a previously undetected strong $\Delta\nu_4 = -\Delta\nu_5 = \pm 2$ Darling-Dennison (DD) resonance transferring intensity from the bright *trans*-bend, ν_4' to the dark *cis*-bend, ν_5' .⁵ Reassignment of entire progressions is possible because ν_1' is accidentally almost equal to $\nu_2' + 2\nu_5'$. If both ν_4' and ν_5' are

excited, the individual vibrational angular momenta ℓ_4' and ℓ_5' couple to produce the total vibrational angular momentum, $\ell'' = \ell_4' + \ell_5'$, and there will be more than one combination of ℓ_4' and ℓ_5' with the same value of ℓ'' . States of common point group symmetry differing only in the quantum numbers ℓ_4' and ℓ_5' are mixed by $\Delta\ell_4 = -\Delta\ell_5 = \pm 2$ vibrational- ℓ -resonance.⁶ We tested the DD bend resonance hypothesis by looking for the vibrational- ℓ -resonance which accompanies simultaneous excitation of both bending vibrations in the SEP spectrum.

Using $K' = 1$ rotational levels of the $\tilde{A}\ 2\nu_3'$ state as SEP intermediates, we recorded high resolution (0.1 cm^{-1}) fluorescence dip SEP spectra of acetylene in the \tilde{X} -state $E_{\text{VIB}} = 7000\text{ cm}^{-1}$ region containing the (0,1,0,8,0) and (0,1,0,6,2) DF peaks.⁷ On the DD resonance hypothesis, vibrational- ℓ -resonance will spread the (0,1,0,8⁰,0⁰)⁰ intensity across two $\ell'' = 0$ levels, (0,1,0,6⁰,2⁰)⁰ and (0,1,0,6 ^{± 2} ,2 ^{∓ 2})⁰, and the (0,1,0,8²,0⁰)² intensity among three $\ell'' = 2$ levels (0,1,0,6²,2⁰)², (0,1,0,6⁰,2²)², and (0,1,0,6 ^{± 4} ,2 ^{∓ 2})², yielding an "extra" $\ell'' = 2$ level. A low resolution (1.0 cm^{-1}) SEP spectrum using the $Q(5)$ PUMP transition with parallel PUMP and DUMP laser polarizations is shown in Fig. 1. The SEP experiment is similar to that described in Ref. 3 and will be described completely elsewhere.⁸ All of the transitions in Fig. 1 have been proven to be downward (rather than upward) by rotational term value coincidences between SEP spectra recorded *via* different intermediate rotational levels. $\ell'' = 2$ levels can readily be distinguished from $\ell'' = 0$ levels because they occur in nearly degenerate pairs of opposite parity at low J .

Vibrational band origins and rotational constants for all observed transitions are listed in Table I and may be compared to predicted zero order rotational constants $B_v^0 = B_0 - \Sigma\alpha_v\nu_i$.⁹ The assignment of the (0,1,0,8,0) level in the dispersed fluorescence spectrum is confirmed by both the rotational constant and the strong rotational- ℓ -resonance between $\ell'' = 0$ and the e parity component of $\ell'' = 2$. Above $J = 4$, transitions to $\ell'' = 4$ are detectable, mainly due to rotational- ℓ -resonance. The off-diagonal rotational- ℓ -resonance matrix element between $\ell = 0$ and $\ell = 2$ e basis states, is (in the parity basis)

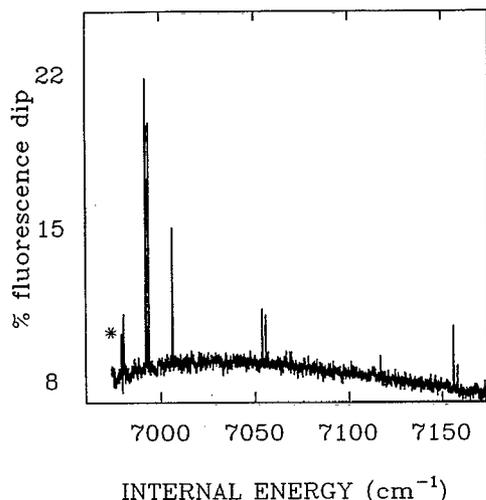


FIG. 1. Low resolution (1 cm^{-1}) SEP spectrum recorded with the $\tilde{A} 2\nu_3$ $J_{K_a K_c} = 5_{1,5}$ intermediate [$Q(5)$ PUMP transition]. The starred transition is an axis-switching transition to the $J=5$, $\ell''=1$ e parity component of $(0,2,0,5^1,0^0)^1$. The levels centered about 6990 cm^{-1} are $J=4$, $\ell''=2f$, $J=5$, $\ell''=2e$, $J=5$, $\ell=0$, and $J=6$, $\ell''=2f$ of $(0,1,0,8,0)$. The levels near 7055 cm^{-1} are $J=5$, $\ell''=2e$ and $J=5$, $\ell''=0$ of $(0,1,0,6^{\pm 2,4}, 2^{\mp 2})^{0,2}$. The level at 7117 cm^{-1} is $J=5$ of $(0,0,1,5^{\pm 1}, 1^{\mp 1})_+^0$, and the levels at 7160 cm^{-1} are $J=5$, $\ell''=0$ and $J=5$, $\ell''=2e$ of $(0,1,0,6^0, 2^{0,2})^{0,2}$. The unusual intensity ratios between the Q branch transitions to $\ell''=0$ and 2 of $(0,1,0,8,0)$ and $(0,1,0,6^{\pm 2,4}, 2^{\mp 2})^{0,2}$ are due to rotational- ℓ -resonance and the saturation of $(0,1,0,8,0)$.

$$V = \frac{\sqrt{2}}{4} q_t \sqrt{(v_t - \ell_t)(v_t + \ell_t + 2)} \times \sqrt{J(J+1)[J(J+1) - 2]}, \quad (1)$$

where q_t is the rotational- ℓ -resonance constant for bending mode $t=4$ or 5 and $\Delta\ell_t = +2$. The rotational- ℓ -resonance matrix element increases roughly linearly with v_t'' and is a measure of bend excitation. (Note that the f parity com-

TABLE I. Band origins, rotational constants, and assignments.

Band origin ^a	ℓ''	B_v	$(v_1, v_2, v_3, v_4^A, v_5^S)^{\ell'}$
7122.74(2)	2	1.1799(4) ^b	$(0106^0 2^2)^2$
7120.68(1)	0	1.1799(4) ^b	$(0106^0 2^0)^0$
7094.78(2)	2	1.1752(3)	$(0015^1 1^1)^2$
7081.26(1)	0	1.1797(4) ^b	$(0015^1 1^{-1})_+^0$
7075.89(3)	2	1.1797(4) ^b	$(0015^3 1^{-1})^2$
7065.05(2)	2	1.1819(2)	$(0106^2 2^0)^2$
7034.59(4)	0	1.1595(5) ^b	$(0302^0 0^0)^0$
7031.69(4)	2	1.1595(5) ^b	$(0302^0 0^0)^2$
7020.53(1)	0	1.1823(3) ^b	$(0106^2 2^{-2})_+^0$
7018.83(2)	2	1.1823(3) ^b	$(0106^4 2^{-2})^2$
6957.94(1)	0	1.1814(4) ^b	$(0108^0 0^0)^0$
6956.56(1)	2	1.1814(4) ^b	$(0108^0 0^0)^2$
6952.67(5)	4	1.179(1)	$(0108^4 0^0)^4$
6944.16(3)	1	1.1624(5) ^c	$(0205^1 0^0)^1$
6939.9(1)	3	1.168(1)	$(0205^3 0^0)^3$

^aBecause of uncertainties in the \tilde{A} -state term values, the vibrational origins have an absolute (2σ) accuracy of $\pm 0.2 \text{ cm}^{-1}$.

^bRotational constants for $\ell''=0$ and 2 constrained to be equal.

^c $\ell''=1$ e parity component should be compared to the effective rotational constant $B_{\text{eff}} = B_v - \frac{1}{4}q_4(v_4 + 1)$ due to rotational- ℓ -doubling (Refs. 4 and 14).

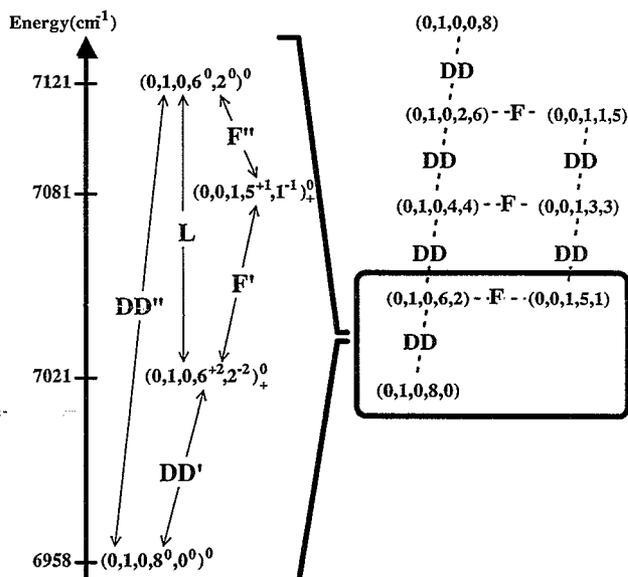


FIG. 2. Interaction diagram for observed Σ_g^+ , $J=0$ levels showing the anharmonic coupling due to Fermi, Darling-Dennison, and vibrational- ℓ -resonance. The observed levels are further coupled to unseen sets of levels at higher energy by the same interactions as specific in the inset. The matrix elements coupling the observed levels are $DD' = \sqrt{3}(r_{45} + 2g_{45})$; $DD'' = 4s_{45}$; $L = 4\sqrt{3}r_{45}$; $F' = -(1/\sqrt{2})K_{2345}$; $F'' = -(\sqrt{6}/4)K_{2345}$. The spectroscopic constants s_{45} , r_{45} , g_{45} , and K_{2345} are defined in Ref. 6.

ponent of $\ell=2$ cannot be perturbed by Σ_g^+ $\ell=0$ levels.) The level shifts due to rotational- ℓ -resonance can be accurately predicted by a slight refinement of Pliva's spectroscopic constants.^{6(a)} The Franck-Condon bright $(0,3,0,2,0)$ vibrational state can be unambiguously assigned from its rotational constant, vibrational band origin, and weak rotational- ℓ -resonance.

The observation of two more $\ell''=2$ levels than $\ell''=0$ levels (e and f parity components of an $\ell''=2$ level are not counted separately) is the key to the vibrational assignment of the remaining states. If only one bending vibration is excited, the number of observed $\ell''=0$ levels must equal or exceed the number of $\ell''=2$ levels. The observation of two "extra" $\ell''=2$ levels is strong evidence that the $(0,1,0,6,2)$ levels and another set of levels, which also involves simultaneous excitation of both the *trans*- and *cis*-bending vibrations, appear in the spectrum.

The $(0,0,1,5,1)$ set of levels is the only set of g symmetry levels with excitation in both *trans*- and *cis*-bending modes predicted to lie within 100 cm^{-1} of the observed levels. $(0,0,1,5,1)$ has one Σ_g^+ $\ell''=0$ sublevel, $(0,0,1,5^{\pm 1}, 1^{\mp 1})_+^0$, and two $\ell''=2$ 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 $\Delta v_3 = -\Delta v_2 = -\Delta v_4 = -\Delta v_5 = \pm 1$, $\Delta\ell_4 = -\Delta\ell_5 = \pm 1$ ("2345") Fermi resonance. This resonance causes the well-known perturbation of the fundamental ν_3' .¹⁰ The resonances among the observed $J=0$ Σ_g^+ levels are illustrated in Fig. 2. We have assigned the level at 7081 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 rotationally allowed SEP transitions in Table I. Complete details of the vibrational analysis will be published shortly.¹¹

In many cases, the magnitude of the rotational- ℓ -resonance between $\ell''=0$ and $\ell''=2$ e sublevels allows assignment of the change in ℓ' between $\ell''=0$ and $\ell''=2$ sublevels of a vibrational state as due predominantly to ℓ'_4 or ℓ'_5 . In particular, the rotational- ℓ -resonance between the $\ell''=0$ and $\ell''=2$ levels at 7120 cm^{-1} is too weak for a $\Delta\ell_4=2$ interaction with $v_4=6$, ruling out the (1,0,0,6,0) CH stretch assignment for this level; thus this level is assigned to (0,1,0,6,2). All higher members of the DF progressions which include (0,1,0,6,2) can now be securely assigned as (0, v_2 ,0, v_4 ,2) appearing through strong DD resonance with [0, v_2 ,0,(v_4+2),0].

The overall pattern of energy levels and ℓ_4/ℓ_5 labels in Table I is qualitatively consistent with diagonalization of a complete FERMI/DD/vibrational- ℓ -resonance Hamiltonian using literature values for the Fermi-resonance¹⁰ and vibrational- ℓ -resonance constants⁶ and a DD resonance constant $|s_{45}| \approx 10\text{ cm}^{-1}$ deduced from the DF intensities. In these calculations, the ℓ_4/ℓ_5 labels lose some of their meaning due to the vibrational- ℓ -resonance, which may explain why the effective rotational- ℓ -resonance matrix element for the level at 7121 cm^{-1} is 40% larger than predicted by a calculation for $\Delta\ell_5=2$ with $v_5=2$: The discrepancy probably results from the separate treatment of rotational- ℓ -resonance instead of a global fit.

The DD resonance between bending vibrations, when combined with the observed vibrational- ℓ -resonance, and 2345 Fermi resonance, provides an IVR pathway from the mv_2+2nv_4 SEP bright states to overtones of v_3 . If the DD resonance between CH stretching vibrations is also considered, *none* of the normal mode quantum numbers will be conserved. However, a resonance vector analysis¹² shows that the total stretching quantum number $n_s=(v_1+v_2+v_3)$, the total vibrational angular momentum ℓ , and a quantum number representing the "resonance condition" that levels have approximately the same energy, $n_{\text{res}}=(5v_1+3v_2+5v_3+v_4+v_5)$, are good quantum numbers for the short-time dynamics. At high energy, these IVR pathways can transfer essentially all the vibrational energy out of the Franck-Condon bright vibrational modes v'_2 and v'_4 on a timescale of a few hundred femtoseconds. Weaker resonances characteristic of longer time dynamics⁵ allow SEP to sample the full symmetry allowed density of states.

Above $J=2$, the starred transition in Fig. 1 is observed, but only *via* qQ branch DUMP transitions in rQ_0 branch PUMPed SEP spectra. It is absent in rR_0 PUMPed SEP spectra. The effective rotational constant and vibrational band origin agree within error with predicted values for the e parity component of (0,2,0,5¹,0⁰).¹ This assignment has been confirmed by SEP spectra recorded *via* $K'=0$ rotational levels. For $J \geq 5$, $\Delta K=2$ oQ , and oP branch DUMP transitions to (0,2,0,5³,0⁰)³ appear in rQ_0 PUMPed SEP spectra as well. The effective ℓ'' splitting constant, g_{44} , for the (0,2,0,5,0) level is halfway between the effective g_{44} constants for (0,1,0,8,0) and (0,3,0,2,0). This strong v_2 dependence of the effective g_{44} constant is remarkable and

may partially explain the difficulties encountered by Strey and Mills in their calculation of the anharmonic force field.⁹

In a bent \rightarrow linear transition, the axis-switching mechanism of Hougen and Watson¹³ leads to the appearance of new vibrational bands which are, in essence, forbidden only by the rotational selection rules. For the rQ_0 branch SEP PUMP transitions used here, if laser polarization effects are taken into account, the forbidden $\Delta K=0$ qQ branch DUMP transitions should be more intense than the allowed pR transitions, such as the pR SEP transition that appears next to the forbidden starred qQ transition in Fig. 1. A well understood constructive interference effect makes the forbidden qQ branch roughly nine times stronger than the other axis-switching branches in the high J limit.¹³ The (0,2,0,5,0) level is Franck-Condon bright from the \tilde{X} -state $K'=0,2$ rotational character mixed into $K'=1$ of $\tilde{A} 2v'_3$ by the axis-switching effect, which is a likely explanation for the forbidden rotational transitions to (0,2,0,5,0). The rotational sub-band intensities are completely consistent with the predictions of the axis-switching mechanism. Nearly 10% of the vibrational bands observed in the SEP spectrum of the isoelectronic molecule HCN can be attributed to axis switching.¹⁴

Both the rotational and vibrational intensities in the SEP spectrum of Fig. 1 are unusual. In the DF spectrum from the same upper state, emission to (0,1,0,8,0) is ten times as intense as (0,1,0,6,2); in the absence of saturation the intensity ratio in the SEP spectrum should be 10 to 1 instead of the observed 5 to 1 ratio. Calculated rotational intensities indicate that the transition to (0,1,0,8,0) $J''=5$, $\ell''=2$ should be 30 times stronger than the transition to $J''=4$, $\ell''=2f$ in Fig. 1, instead of just five times as strong. We have checked the linearity of our SEP detection and the reproducibility of the observed intensities. The observed intensity orderings agree with calculations and calculated intensity ratios are accurate for the weaker lines. Part of the explanation for the above intensity anomalies is that the stronger transitions are saturated, with half-widths approximately twice those of the weaker transitions.¹⁵ The situation is more complex than simple saturation because the sharp downward SEP transitions compete with a continuum of upward transitions,¹⁶ which is also the principle source of noise in our SEP spectra.

A tenfold increase in resolution between low (1.0 cm^{-1}) and high resolution (0.1 cm^{-1}) SEP nearly matches the Doppler and laser linewidths, so that high resolution SEP has about a tenfold higher signal-to-noise ratio, allowing the observation of the weaker transitions to levels listed in Table I but not discernible in Fig. 1. An estimate for the intensity ratio between the strongest and weakest detected SEP transitions of about 500 has been obtained as follows: Calculated rotational line intensities are used to determine the ratio between saturated and unsaturated rotational lines for the stronger vibrational transitions; observed intensity ratios are used to compare unsaturated weak rotational transitions of the strong vibrational transitions to the weakest vibrational transitions. A 500-fold range of detectable SEP transitions is

surprising, given that the largest observed fluorescence dip in these experiments is about 14% and the detection limit is somewhat less than 0.5%. Since it is not uncommon to observe 30% fluorescence dips, the range of detectable SEP intensities is probably about 1000!

Taken together, the resonances shown schematically in Fig. 2 and forbidden rotational transitions provide a possible explanation why the symmetry-sorted density of states observed by SEP exceeds the symmetry-sorted, ℓ -sorted density of states from anharmonic direct counts.³ The ℓ -sorting procedure used on the 15 000 cm^{-1} data set essentially identified $\ell''=2$ levels by the expected and observed near degeneracy between opposite parity components at $J''=2$ and assumed $J''=1$, $\ell''=0$ quantum numbers for the remaining levels. In retrospect, the latter assumption seems naive: Forbidden rotational transitions could have contaminated the $\ell''=0$ sequence. The observed density of vibrational levels in the $\ell''=2$ sequence, $\rho_{\text{VIB}} \approx 0.5/(\text{cm}^{-1})$, is about half the calculated value from an anharmonic direct count, $\rho_{\text{VIB}} \approx 1.0/(\text{cm}^{-1})$.

The "extra" $\ell''=2$ levels observed by Chen *et al.* at 12 840 cm^{-1} are explained by the vibrational- ℓ -resonance among states with excitation in both degenerate bending vibrations reported here. All of the states observed in the region between 9400 cm^{-1} and 9700 cm^{-1} by Abramson *et al.*² 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. *This recognition of the importance of axis-switching transitions and dominant \tilde{X} -state resonances has already led to conclusive assignment of all unassigned states in the SEP spectrum of HCN and a substantial reinterpretation of the vibrational dynamics of acetylene.* Since it is apparently quite common to observe extremely weak allowed rotational transitions in SEP spectra, and saturated fluorescence dips of 30% are not uncommon, the high sensitivity of SEP demonstrated here should have valuable consequences for the analysis of IVR in other molecules.

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