

# Long-Range, Resonant Vibrational Energy Exchange in Polyatomic Molecules: The Fundamental Acetylenic CH Stretching Spectrum of $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$

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The 3.0- $\mu\text{m}$  spectrum of triethynylmethylsilane,  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ , was recorded with optothermal detection of a skimmed molecular beam. Both bands that occur in this region, the totally symmetric acetylenic CH stretch ( $\nu_1$ ) and the asymmetric acetylenic CH stretch ( $\nu_{13}$ ), have lifetime broadened line shapes corresponding to an IVR lifetime of 350 and 490 ps, respectively. The splitting between the band centers of the symmetric and asymmetric CH stretches was measured to be  $0.171 \pm 0.026 \text{ cm}^{-1}$  and determines the time for excitation localized on one CH stretch to tunnel to the other symmetrically equivalent bonds. Direct resonant dipole-dipole coupling predicts a splitting 4.7 larger than observed and, with the effect of induced dipole moments, should increase the splitting even further. To shed light on this anomaly, we examine the equivalent splitting in diacetylene, using the *ab initio* force field to help separate different contributions. Conjugation plays a dominate role in determining the diacetylene splitting, but it appears unlikely that this mechanism is important for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ .

## Introduction

Long-range electronic energy transfer is a well-studied and important topic in chemical physics, playing key roles in such fundamental process as photosynthesis. Electronic energy transfer manifests itself in the spectra of organic crystals as splittings due to exciton hopping, driven by dipole-dipole (or higher multipole) couplings.<sup>1</sup> Long-range electron transfer often occurs via non-resonant excitation of the chemical bonding network via processes such as superexchange.<sup>2</sup>

Little is known about the equivalent vibrational energy transfer processes in polyatomic molecules. This has been in part due to the widely held belief that intramolecular vibrational energy relaxation (IVR) would occur in a few picoseconds or less in all polyatomic molecules, thus preventing long-range vibrational exciton hopping, except perhaps for groups like CO with very large transition dipole moments. Recent work in several laboratories has shown that, in the region of the CH stretching fundamentals and first overtone bands, IVR lifetimes are typically hundreds of picoseconds to several nanoseconds.<sup>3-5</sup> This means that even weak couplings can lead to resonant energy transfer before relaxation.

In this paper we report the high-resolution infrared spectrum of what we hope will be the first of several studies of the spectra of molecules with equivalent terminal acetylene groups. Coupling between the equivalent groups leads to a splitting of the fundamental frequencies between normal modes of different symmetry with the same type of excitation (the acetylenic CH stretching mode here). Such a splitting of the fundamentals has traditionally been interpreted in terms of different force constants for the different symmetry species, and ultimately a coupling force constant. Theoretical work on  $\text{XH}_n$  molecules, such as that by Halonen and Child,<sup>6</sup> has shown that the splittings between the overtone and combination bands of equivalent X-H stretches are often more adequately described by local, instead of normal, mode theory. Halonen and Child have shown that the ratio of bond anharmonicity over the net coupling between equivalent bonds ( $\omega_{\text{Xc}}/\lambda$ ) determines whether a molecule displays a local or harmonic normal mode spectrum. For  $\omega_{\text{Xc}}/\lambda \gg 1$  the molecule is in the local mode limit, and for  $\omega_{\text{Xc}}/\lambda \ll 1$  the motion is more adequately described by normal modes. For  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ , based on the results presented below, this ratio is on the order

of 1000, indicating that the molecule is in the extreme local mode limit. However, in the fundamental region there is little difference between the symmetrized local mode and the normal mode wave functions, although they suggest different dynamics since they represent qualitatively different classical motions. In the local mode model, it is natural to interpret the splitting between equivalent bonds dynamically, as the time it takes for the excitation, initially localized on one bond, to transfer to one of the other symmetrically equivalent bonds.

To better understand the observed splitting in  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ , we also examine the splitting of the symmetric and antisymmetric CH modes in diacetylene. For this molecule, the splitting is known from experiment and the force field from *ab initio* calculations. This allows us to separate out different contributions to the splitting, which is not possible for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  at this time.

## Experimental Section

Triethynylmethylsilane was prepared from  $\text{CH}_3\text{SiCl}_3$  [Aldrich] and  $\text{HC}\equiv\text{CMgCl}$  [Aldrich] in tetrahydrofuran according to the procedures outlined in ref 7. The final product was 77% pure by  $^1\text{H}$  NMR. The impurity, THF, caused no complications in the recording of the spectrum since its infrared absorptions occur at a different frequency than the compound of interest.

The spectrometer, which was described in detail earlier,<sup>3a</sup> consists of a continuously scanning continuous wave 3.0- $\mu\text{m}$  color center laser [Burleigh] and a molecular beam machine with bolometer detection. Helium gas passed, at various backing pressures, over a room-temperature liquid sample of  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ . The gas line leading into the machine was at 90 °C and the 50  $\mu\text{m}$  diameter nozzle at 120 °C. Above 50 psi He backing pressures, severe clustering was observed as a negative signal from the bolometer. This is caused by predissociating species leaving the molecular beam path upon absorption of radiation. Only slight clustering occurred at 30 psi of He, and the spectrum taken at this pressure was used for the analysis. We used two high-finesse etalons (7.5 GHz and 150 MHz free spectral range) to monitor and linearize the laser frequency. The instrumental line width of our spectrometer is approximately 8 MHz, due to slightly nonorthogonal crossings of the laser with the molecular beam. An absorption spectrum of acetylene in a gas cell was recorded along with the bolometer signal and was combined with published frequencies<sup>8</sup> to establish an absolute frequency calibration of the spectrum.

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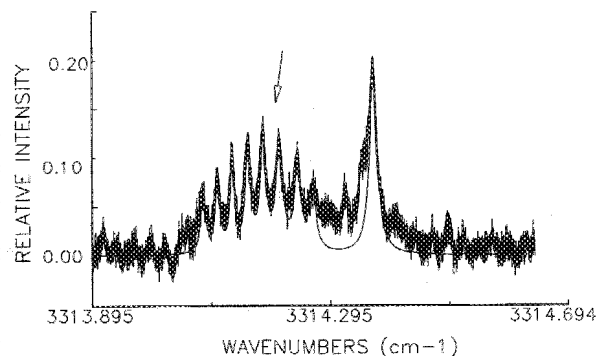


Figure 1. The 3.0- $\mu\text{m}$  spectrum of  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  taken with optical detection of a skimmed molecular beam, resulting in a 10-MHz instrumental line width. The several hundred megahertz broadening of the features is homogeneous broadening due to the IVR lifetime of the initially excited CH stretch. On the high-energy side is the Q branch of the  $\nu_1$  band, and lower in energy is a series of perpendicular Q branches for the  $\nu_{13}$  band (the band center for  $\nu_{13}$  is marked with the arrow).

### Results and Discussion

The rotational constants for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  were calculated by assuming standard bond lengths, tetrahedral angles around the Si atom, and linear acetylene groups. The results predict this molecule to be a slightly oblate top with  $A = B = 1.53$  GHz and  $C = 1.11$  GHz. Sacher, Davidsohn, and Miller found  $C_{3v}$  symmetry to be consistent with the IR and Raman spectra measured by them.<sup>9</sup> In the 3.0- $\mu\text{m}$  region, the spectrum should consist of two bands: the totally symmetric acetylenic CH stretch  $\nu_1$  ( $A_1$  symmetry showing a parallel-type transition) and the asymmetric CH stretch  $\nu_{13}$  ( $E$  symmetry exhibiting a perpendicular-type transition). Figure 1 shows the high-resolution, infrared spectrum for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  in the 3.0- $\mu\text{m}$  region. On the high-energy side is a parallel band Q branch, which we take as the origin of the  $\nu_1$  totally symmetric fundamental at 3314.367  $\text{cm}^{-1}$ . This Q branch is well approximated by a Lorentzian line shape with a full width at half-maximum of 450 MHz. The P and R branches are not observable due to the low signal to noise ratio of the spectrum.

Lower in energy are a series of perpendicular Q branches of the  $\nu_{13}$  band. The separation between these Q branches should be  $2^*(B-C)$ , which is calculated to be about 840 MHz compared to the average experimentally observed value of 780 MHz (0.026  $\text{cm}^{-1}$ ). The origin of the  $\nu_{13}$  band is halfway between the  $K = 0 \rightarrow 1$  and  $K = 1 \rightarrow 0$  Q branches and was assigned to be at 3314.196  $\text{cm}^{-1}$  (shown by the arrow in Figure 1). The assignment of these Q branches could be off by at most  $\pm 1$  unit, leading to an uncertainty in the  $\nu_{13}$  fundamental band origin of  $\pm 0.026$   $\text{cm}^{-1}$ . This assignment, although tentative, was based upon the rotational temperature of the beam and the expected nuclear spin statistics. The small number of Q branches in the spectrum, combined with the very small rotational constants for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ , shows that the rotational temperature in the beam is less than 1 K, and thus the smallest  $K$ s are the most populated. This temperature is considerably lower than the  $\sim 5$  K temperature typically observed in this machine. The spin statistical weights for this molecule are 24:20 for  $K = 3N$  versus  $K = 3N \pm 1$ , assuming a rigid  $C_{3v}$  conformation.

Spectra with Lorentzian line shapes, broadened not by the instrumental line width but by the IVR lifetime of the initially created state, have been observed previously in our laboratory for molecules with a very large density of states.<sup>3a,b</sup> The density of states for this molecule was estimated in the harmonic approximation by taking the inverse Laplace transform of the partition function.<sup>10</sup> Normal mode frequencies reported by Sacher et al.<sup>9</sup> were used, and the frequencies of the two  $A_2$  symmetry modes they did not report are estimated from the corresponding modes in  $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$  (350  $\text{cm}^{-1}$  for  $\nu_{11}$  the  $\text{SiC}\equiv\text{C}$  bend and 190  $\text{cm}^{-1}$  for  $\nu_{12}$  the  $\text{CH}_3$  torsion).<sup>12</sup> The total density of vibrational states at 3314  $\text{cm}^{-1}$  is approximately  $1.1 \times 10^5/\text{cm}^{-1}$

TABLE 1: Summary of Results from the 3.0- $\mu\text{m}$  Spectrum of  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$

band	tentative <sup>a</sup> assignmt ( $^{\Delta K}\Delta J_{K''}$ )	position <sup>b</sup>	rel intens <sup>c</sup>	full width at half-max (MHz) <sup>d</sup>
$\nu_1$	QQ	3314.3671	0.191	454
$\nu_{13}$	$^PQ_3$	3314.265	0.067	382
	$^RQ_2$	3314.2394	0.095	400
	$^PQ_1$	3314.2091	0.112	378
	$^RQ_0$	3314.1822	0.122	348
	$^RQ_1$	3314.1566	0.116	298
	$^RQ_2$	3314.1301	0.104	256
	$^RQ_3$	3314.1055	0.078	268
	$^RQ_4$	3314.082	0.062	285

<sup>a</sup> As discussed in the text, the assignments of the features in  $\nu_{13}$  are tentative and may be off by  $\pm 1$  K assignment. <sup>b</sup> The uncertainty in position is estimated to be  $\pm 0.0005$   $\text{cm}^{-1}$  except for  $^RQ_3$  and  $^RQ_4$  where the uncertainty is larger due to the very low  $S/N$ . <sup>c</sup> The uncertainty in the intensity for the fit shown in Figure 1 is approximately  $\pm 0.003$ . <sup>d</sup> The uncertainty in the width for the fit is approximately  $\pm 2$  MHz.

of which  $1/6$  should be of  $A_1$  symmetry and  $1/3$  of  $E$  symmetry.<sup>13</sup> In this calculation, the torsional mode is treated as a harmonic oscillator, but in our earlier work on  $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$ ,<sup>3a</sup> we found only a modest increase in the density of  $A_1$  states when the torsional mode was treated explicitly as a hindered internal rotation and the vibrational states classified according to the appropriate molecular symmetry group,  $G_{162}$ . For the parallel band, the density of  $A_1$  symmetry states that can couple via anharmonic interactions will thus be on the order of  $1.8 \times 10^4/\text{cm}^{-1}$ , while for the perpendicular band the density of  $E$  symmetry states that can anharmonically couple should be twice as large. If the torsional tunneling splittings are resolved in the spectrum due to interaction with bath states with multiple quanta in the torsional mode, the density of lines expected in the spectrum will increase by a factor of 3 in both cases.

The observed Q branches were fit to Lorentzian line shapes in the following manner. First, the parallel band Q branch at 3314.3671  $\text{cm}^{-1}$  was fit separately from the rest of the spectrum without including the additional absorptions centered at 3314.351  $\text{cm}^{-1}$  and at 3314.321  $\text{cm}^{-1}$ . These features could be combination bands, as observed previously on the low-frequency side of Q branches in the  $(\text{CX}_3)_3\text{YC}\equiv\text{CH}$  series.<sup>3b</sup> The perpendicular band Q branches were fit simultaneously to Lorentzian line shapes by a linear least-squares analysis, including the parallel band Q branch but holding the parameters of the latter constant. Figure 1 shows the results of the fit, and Table 1 lists the parameters determined by the fit.

From the width of the Lorentzian line shapes a lifetime can be extracted according to the formula  $\tau = 1/(2^*\pi^*\Delta\nu)$ , where  $\Delta\nu$  is the full width at half-maximum of the Lorentzian line shapes. For the  $\nu_1$  fundamental the Q branch line width is 450 MHz, which corresponds to an upper-state lifetime of 350 ps. For the  $\nu_{13}$  fundamental the line widths of the features vary from 400 to 256 MHz. Taking the average line width (327 MHz), we predict a lifetime of 490 ps. Given the low temperature of the expansion, coupled with the small change in rotational constants expected, inhomogeneous contributions to these widths are likely negligible. It is interesting that the two lifetimes differ, given their great similarity of motion. Stuchebrukhov and Marcus have calculated the IVR relaxation rate of the related series of molecules,  $(\text{CX}_3)_3\text{YC}\equiv\text{CH}$ , and found that the energy decays through a chain of nonresonant low-order anharmonic couplings.<sup>13</sup> In the present case, it is likely that the symmetry restrictions on the relaxation pathways for the two normal mode states are responsible for the difference in the lifetimes. Additionally, both lifetimes for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  are significantly shorter than the corresponding lifetime of  $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$ , which is 2000 ps.<sup>3a</sup> It has been proposed that internal rotation acts as an accelerator for IVR,<sup>14</sup> yet in the present case the molecule with three methyl groups  $(\text{CH}_3)_3\text{Si}(\text{C}\equiv\text{CH})_3$  relaxes slower than a very similar molecule with only one methyl group  $(\text{CH}_3\text{Si}(\text{C}\equiv\text{CH}))_2$ .

From the splitting of the two CH normal modes, the time it takes for one quantum of excitation to hop from one CH stretch to the other two symmetrically equivalent CH stretches and back can be calculated. If at time  $t = 0$  the molecule has bond 1 excited, then as a function of time the probability that the same bond is still excited is given by

$$|(1|\psi(t))|^2 = \frac{1}{9} \left[ 5 + 4 \cos\left(\frac{6\pi\lambda t}{\hbar}\right) \right] \quad (1)$$

The probability of having the vibrational energy in bond 1 oscillates between 1 and  $1/9$ , with a frequency  $f = 3\lambda/\hbar$ , where  $3\lambda$  represents the splitting between the levels in energy units ( $f = 3\lambda c$  if the splitting is given in wavenumbers). Similarly, the probability of the excitation being in bond 2 (or 3) oscillates between 0 and  $4/9$ , with the same frequency. The measured splitting of  $0.171(26)$   $\text{cm}^{-1}$  implies that the time for the excitation probability to go from a maximum to a minimum is  $31(5)$  ps. This energy hopping rate is about a factor of 10 faster than the rate of IVR.

The splittings between the A and E fundamentals can be calculated from the force constant and the kinetic coupling between the equivalent bonds (terms from the Wilson F-G matrices). As the equivalent bonds become farther apart in the molecule, the force constant dominates the interaction, since the kinetic coupling is expected to decrease exponentially with the number of intervening bonds. One component of the interaction force constant between two bonds is dipole-dipole coupling with other contributions from electronic rearrangement or polarizability. Considering first the dipole-dipole coupling to be the predominant coupling mechanism allows a splitting between the  $\nu_1$  and  $\nu_{13}$  band origins to be calculated. The interaction potential between two dipoles is

$$V = \frac{1}{4\pi\epsilon_0} \left[ \frac{\mu_1 \cdot \mu_2}{r^3} - 3 \frac{(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5} \right] \quad (2)$$

where  $r$  is the distance between the two dipoles. The factor of  $4\pi\epsilon_0$  is present in SI units, not in Gaussian (esu) units. Assuming equivalent dipoles and the tetrahedral angles between them reduces this to

$$V = +\frac{5}{3} \frac{1}{4\pi\epsilon_0} |\mu_1|^2 / r_{12}^3 \quad (3)$$

Placing the dipole moment on the center of each CH bond results in a  $r_{12}$  of  $5.85 \text{ \AA}$ . The effective resonant dipole-dipole coupling between two local mode vibrationally excited states can be calculated from the same formula with the dipole operator replaced by the vibrational transition dipole moment for the local mode. Assuming a canonical value for the acetylenic CH stretch transition dipole moment of  $0.08 \text{ D}^{15}$  results in a dipole-dipole coupling matrix element of  $0.268 \text{ cm}^{-1}$ . The splitting of the A and E fundamentals will be 3 times this coupling matrix element between the local modes. Therefore, the splitting is calculated to be  $+0.804 \text{ cm}^{-1}$  compared to the measured value of  $+0.171 \text{ cm}^{-1}$  (the order of the bands is correctly predicted). Thus, direct dipole-dipole coupling predicts a splitting 4.7 times as large as the experimentally measured one. Attempts to improve the model by distributing the dipole over the acetylenic chromophore would only decrease the effective interaction distance and make the predicted splitting even larger.

Because of the large polarizability of the  $\pi$  electrons in the  $\text{C}\equiv\text{C}$  bond, we at first suspected that some type of "shielding" effect was responsible for reducing the splitting expected from the direct dipole-dipole interaction alone. Two charge distributions interacting in an isotropic dielectric medium have their interaction energy reduced by the dielectric constant. However, here the molecular polarizability is not isotropic but located between the two interacting dipoles. With the polarizability of the  $\text{C}\equiv\text{C}$  bond taken from the polarizability of acetylene, it is

estimated that the transition dipole on one  $\text{C}\equiv\text{C}-\text{H}$  will induce a dipole of about 5% as large in the other  $\text{C}\equiv\text{C}$  bonds. These small dipoles are much closer to their adjacent  $\text{C}\equiv\text{C}-\text{H}$  bonds, and in the opposite direction, and thus lead to an enhancement of the dipole-dipole coupling of about 1 order of magnitude. The point dipole approximation is likely not valid for adjacent bonds, but a substantial reinforcement of the direct dipole-dipole coupling should result no matter how the dipole is distributed on the  $\text{C}\equiv\text{C}$  bond. Thus, including the polarizabilities of the triple bonds dramatically increases the disagreement of the electrostatic prediction with our experimental observations.

An enhancement of the electrostatic interactions of two oppositely charged monopoles when a dielectric sphere is placed between them was noted by Buckingham.<sup>16</sup> Buckingham states that there is no effect on the interaction energy of two charges of the same sign when a dielectric sphere is placed halfway between them. However, one charge and the dielectric sphere have an attractive interaction (due to the induced dipole moment). Bringing up another equal charge on the opposite side of the sphere cancels that attraction in addition to the direct Coulomb repulsion between the charges. As a result, the effective repulsive interaction of the two like charges is also enhanced by the presence of dielectric material between the two charges. Since the interaction of charges, independent of sign, is increased by an intervening dielectric, the same should apply to the interaction of higher electric multipole moments as well, since they can be represented as a collection of point charges.

Resonant dipole-dipole interaction is only one mechanism for the coupling of the local mode oscillators. Nonresonant excitation of the bonds connecting them, similar to superexchange in electron-transfer theory, will also couple the local modes. Superexchange has been postulated as the mechanism for the primary electron-transfer process in photosynthesis where the electron travels  $17 \text{ \AA}$  in  $2.8 \text{ ps}$ .<sup>2</sup> The interaction between adjacent bonds comes from both potential and kinetic coupling. At the harmonic level, the kinetic coupling between the terminal CH groups should be extremely small (a normal mode calculation with only diagonal force constants predicts a splitting of  $\sim 0.01 \text{ cm}^{-1}$ ). Indirect, effective potential coupling between the two end oscillators can come from nonresonant mixing of other modes into the "CH" normal mode. Either or both "superexchange" mechanisms (potential or kinetic couplings through the bonds) could produce a coupling of similar size and opposite sign as the dipole-dipole interaction, producing the anomalously small A, E splitting. Near perfect cancellation of potential and kinetic coupling of bonds occurs in the spectra of  $\text{SiH}_3\text{D}$ ,  $\text{SiH}_4$ , and  $\text{GeH}_4$ , leading to much better local modes than would be expected by consideration of either coupling term alone.<sup>6b</sup> For  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  we need to invoke a cancellation of  $\sim 80\%$  of the direct dipole-dipole interaction, while if the polarizability of the  $\text{C}\equiv\text{C}$  bonds raises the direct potential interaction by something like a factor of 10, we need to invoke a cancellation of  $\sim 98\%$ . Such a fine-tuned cancellation is hardly likely to happen by mere chance. This shows the importance of further studies on other molecules with multiple equivalent acetylene groups.

Diacetylene is the only other molecule with multiple acetylene groups for which an accurate normal mode splitting is known from high-resolution spectroscopy;<sup>17</sup> the  $\nu_1-\nu_4$  splitting (symmetric minus antisymmetric) is  $-1.51 \text{ cm}^{-1}$ . Botschwina has published an *ab initio* harmonic force field for diacetylene.<sup>18</sup> This force field predicts a  $\nu_1-\nu_4$  splitting of  $-0.92 \text{ cm}^{-1}$ , in good accord with the experimental results. This splitting is of the opposite sign from what we expect on the basis of dipole-dipole coupling of the two CH oscillators. Since the force field correctly predicts the observed sign, we can use it to find the dominant contributions to the effective interaction.

The *ab initio* calculation of Botschwina<sup>18</sup> predicts that the dipole derivative for stretching each CH bond in diacetylene is  $0.25$  atomic units, 7% higher than that of HCN calculated at a similar level.<sup>15</sup> The HCN derivative predicts the CH stretch

fundamental intensity in this molecular to a few percent.<sup>19</sup> Thus possible conjugation of the two collinear triple bonds does not significantly affect the CH bond dipoles. This also supports our use of the HCN transition dipole moment for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ . Putting resonant dipoles at the center of the CH bonds in diacetylene (separated by 5.02 Å), we predict a normal mode splitting of +1.30  $\text{cm}^{-1}$ . This is remarkably close in magnitude to the observed value, but of the wrong sign! For this molecule, which has collinear bonds and lacks a heavy central atom, the effect of kinetic coupling down the chain is significant, in contrast to  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ . A calculation of the normal mode frequencies for a force field with only diagonal force constants predicts a  $\nu_1-\nu_4$  splitting of +2.25  $\text{cm}^{-1}$ , which comes completely from through-bond kinetic coupling. The sum of the dipole-dipole coupling plus the kinetic coupling predicts a total splitting of +3.5  $\text{cm}^{-1}$  (instead of the measured -1.51  $\text{cm}^{-1}$ ). Thus either there are other contributions to the direct potential coupling of the local modes, or potential coupling through the chain must be dominating the total splitting.

If we look at the interaction force constant calculated *ab initio*, we find a value of the same sign and about 2.5 times larger than that predicted by the simple dipole-dipole interaction. The coupling is larger, perhaps due to the polarization enhancement discussed earlier. As before, a simple point-induced dipole calculation predicts an enhancement of  $\sim 10$ . Thus the theoretical force field of Botschwina supports our prediction that the polarizability will significantly increase the dipole-dipole interaction of the two acetylenic CH local modes. On the basis of the *ab initio* value of the force constant, and the through-bond kinetic coupling, we predict a splitting of +5.5  $\text{cm}^{-1}$ .

The difference between the splitting calculated from the full harmonic force field, -0.92  $\text{cm}^{-1}$ , and the +5.5  $\text{cm}^{-1}$  predicted from the kinetic and direct potential coupling must come from through-bond potential coupling. Examination of the full *ab initio* harmonic force field shows that while the interaction force constant between the two CH stretches is small and positive (+0.3 N/m), the interaction between the two C $\equiv$ C bonds is large and negative (-23.0 N/m). The CH modes contain sufficient mixing of the C $\equiv$ C modes ( $\Delta R(\text{C}\equiv\text{C})/\Delta r(\text{CH}) = -0.12$ ) for the effective interaction to be dominated by the large negative interaction constant between the C $\equiv$ C stretching coordinates. Changing only this large interaction force constant to zero changes the calculated harmonic splitting of the two normal modes from -0.92 to +0.94  $\text{cm}^{-1}$ . Thus indirect coupling through this C $\equiv$ C interaction force constant dominates the calculated splitting and appears responsible for the observed sign being opposite from that predicted by the dipole-dipole coupling term. This large negative interaction force constant between the two C $\equiv$ C bonds is most likely a consequence of conjugation of the three CC bonds. This conjugation is also reflected in the large positive value (+64.7 N/m) of the interaction force constant between the C $\equiv$ C and C—C bonds. When one C $\equiv$ C bond is stretched, electron density flows to the C—C single bond, causing its bond length to shrink while that of the other C $\equiv$ C lengthens. A spectroscopic consequence of this strong coupling among the three carbon-carbon bonds is that the splitting of the symmetric and antisymmetric C $\equiv$ C stretching fundamentals ( $\nu_2-\nu_3$ ) is large, +162  $\text{cm}^{-1}$ . In  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ , we expect conjugation to be much less important since the triple bonds are no longer collinear and are separated by a Si atom. This is supported by the fact that the symmetric and antisymmetric C $\equiv$ C stretching fundamentals in  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  are unresolved in the low-resolution IR spectrum and are thus likely within a few wavenumbers of each other, unlike the 162- $\text{cm}^{-1}$  splitting for the same bands observed in diacetylene. While the failure of electrostatic calculations to predict the splitting in diacetylene can be rationalized as due to the effects of conjugation, it is not clear why the calculations should be inaccurate for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ .

## Conclusions

The splitting between the symmetric and asymmetric acetylenic CH stretches in  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$  of  $0.171 \pm 0.026 \text{ cm}^{-1}$  reflects an effective coupling between the equivalent  $\equiv\text{CH}$  stretches. This leads to a tunneling time for bond-localized vibrational excitation of 31(5) ps. Dipole-dipole coupling alone predicts a splitting about 5 times larger, and adding polarizability corrections should increase the expected splitting. Some type of through-bond coupling, similar to superexchange, must be responsible for the much smaller observed splitting. The question remains if this is a fortuitous cancellation or some systematic effect.

In diacetylene, Botschwina's *ab initio* force field does a good job of predicting the observed splitting (which is of the opposite sign as predicted by dipole-dipole coupling). The *ab initio* results on diacetylene support the CH transition moment we used in estimating the dipole interaction and demonstrate that the direct potential interaction is in fact enhanced over the dipole-dipole as predicted on the basis of consideration of the polarizability of C $\equiv$ C bonds. The enhancement, a factor of 2.5, is significantly less than that predicted. The observed and calculated inversion of the order of the fundamentals, relative to the prediction based upon both the direct potential and kinetic coupling, is a consequence of conjugation in diacetylene which leads to large interaction force constants between the three CC bonds.

It is unlikely that conjugation is playing a significant role in  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ , and thus the apparent through-bond potential coupling remains unexplained. We hope the present results, which show that even very small, long-range resonant splittings can be measured, will motivate further theoretical calculations on these and similar molecules. Given the success of *ab initio* theory in explaining the observed splitting in diacetylene, one can be optimistic that the high-level theory could do the same for  $\text{CH}_3\text{Si}(\text{C}\equiv\text{CH})_3$ .

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## References and Notes

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