

# Rovibrational spectroscopy of the $v=6$ manifold in $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}_2\text{H}_2$

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We recorded rovibrational spectra of the  $006^+$  level of  $^{12}\text{C}_2\text{H}_2$  and the  $2131\ 1\ 1^{-1}$  level of  $^{13}\text{C}_2\text{H}_2$  in the ground electronic state using a two-photon sequential double resonance technique with a resolution of 15 MHz. Owing to the  $g/u$  symmetry of acetylene, the levels that we observe are inaccessible from the ground state by single photon techniques, and observation of these levels is reported here for the first time. Upper state rotational constants were derived from whole band fits of the observed lines, and compare favorably with expected values. Both spectra exhibit signs of local perturbations, and a density of states analysis leads us to believe that we are observing couplings to the full density of vibrational states one would expect from acetylene in this energy region. Despite the high resolution of our spectrometer, and the high excitation energy, no evidence for acetylene hydrogen permutation exchange isomerization (which is predicted to proceed through the vinylidene minimum on the potential) has been observed, implying that the rate of exchange isomerization is more than four orders-of-magnitude below the rate predicted by RRKM (Rice, Ramsperger, Kassel, and Marcus) theory. © 2000 American Institute of Physics.

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## INTRODUCTION

Acetylene has a very rich overtone spectrum that, over the years, has been extensively studied by many researchers using a variety of spectroscopic techniques.<sup>1–8</sup> Since the number of references is large, we will limit ourselves to pointing out a recent series of articles by Herman *et al.*,<sup>9–14</sup> in which much of the experimental work on both normal and C-13 labeled acetylene has been collected, and where a polyad model (Herman *et al.* refer to the polyad model as a cluster model in their work), based upon a similar model by Kellman,<sup>15,16</sup> has been developed to account for the global vibrational patterns in the ground electronic state.

Acetylene is a small molecule which is computationally tractable, and thus, much is known about its potential energy surface.<sup>17</sup> Its overtone spectrum at high  $v$  is quite complex, with nearly every band exhibiting local perturbations. Further, there exists a quasistable isomer of acetylene—vinylidene—in which both hydrogen atoms are bonded to the same carbon atom, forming a singlet diradical.<sup>18</sup>

To date, there has been no direct experimental detection of acetylene/vinylidene isomerization. The zero point energy of the vinylidene isomer is predicted to be approximately  $15\ 000\ \text{cm}^{-1}$  higher in energy than the acetylene zero point,<sup>19</sup> which is within the range previously studied by both direct

absorption and stimulated emission pumping techniques.<sup>20–22</sup> In addition to many theoretical treatments of the isomerization process,<sup>17,23</sup> there have been a few studies in which energy largely in excess of  $15\ 000\ \text{cm}^{-1}$  has been deposited into acetylene, with no evidence of isomerization.<sup>2–5</sup> In most cases, the bulk of the excitation was deposited into the CH stretching modes. However the transition from acetylene to vinylidene is, from a mechanistic point of view, expected to require significant excitation of the CH bend and CC stretch modes.<sup>24</sup>

One of the motivations for the present study was the investigation of the isomerization issue. In particular, we hoped to witness a unimolecular isomerization reaction *in situ*. One manifestation of isomerization in a frequency domain spectrum would be the appearance of tunneling shifts and splittings associated with permutation of identical atoms. For the case of acetylene, we expected that identical atom permutation splittings would appear in the spectrum. In essence, for the symmetric double well potential energy surface of electronic ground state acetylene, one hydrogen atom can migrate to the other carbon atom, forming vinylidene. However, following this, there is the possibility that the other hydrogen atom will hop back, thus interchanging the two hydrogens. The “hopping” means that energy levels on one side of the potential energy barrier are mixed with levels on the other side. The mixing of acetylene basis states with vinylidene basis states will lead to locally enhanced tunneling splittings. Below the top of the isomerization barrier and far from the domain of influence of a vinylidene level, the hydrogen exchange tunneling doubling will be very small.

In the case of  $^{12}\text{C}_2\text{H}_2$ , due to nuclear spin symmetry

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restrictions, only one component of each tunneling doublet has nonzero weight.<sup>25</sup> This means that tunneling splittings cannot appear in the spectrum, although tunneling shifts could. However, distinguishing a tunneling shift from a perturbation shift in which one component is too weak to be seen, is problematic. For  $^{13}\text{C}_2\text{H}_2$ , in contrast, both components of the doublet have nonzero statistical weights. For states of  $e$ -parity, in the absence of tunneling splitting, the intensity ratio of even:odd  $J$ -levels in di- $^{13}\text{C}$ -acetylene is 10:6. Perturbation by vinylidene states cause the even  $J$ -levels to split into a 9:1 doublet, and the odd  $J$ -levels into a 3:3 doublet. The observation of doublets with these intensity ratios in the overtone spectrum of  $^{13}\text{C}_2\text{H}_2$  would be unambiguous evidence of hydrogen exchange isomerization.

The sub-Doppler double resonance optothermal molecular beam spectrometer, built recently at Princeton, is capable of depositing in excess of 2 eV of vibrational energy into a molecule with an energy resolution of 15 MHz. While the general aim is to carry out eigenstate resolved spectroscopy at chemically relevant energies, in the present study we set out to compare the  $006^+$  level of  $^{12}\text{C}_2\text{H}_2$  with previous results on the  $006^-$  level.<sup>2</sup> In addition, we attempted without success, to find evidence of acetylene–vinylidene isomerization in the  $2131\text{ }^1\text{1}^{-1}$  and  $4111\text{ }^1\text{1}^{-1}$  levels of the  $^{13}\text{C}_2\text{H}_2$  isotopomer. (For details of our notation, see Ref. 26.)

## EXPERIMENT

The optothermal molecular beam spectrometer has been previously described.<sup>27</sup> In brief, a molecular beam is formed by expanding a 1% mixture of acetylene in helium through a  $30\text{ }\mu\text{m}$  nozzle. The expansion is collimated by a  $275\text{ }\mu\text{m}$  conical skimmer located approximately 1 cm downstream, which extracts the centerline portion of the expansion and isolates the high pressure source chamber ( $10^{-4}$  torr) from the low pressure detector chamber ( $10^{-7}$  torr). The molecules are excited to the  $v=6$  manifold of the CH stretching chromophore via a sequential double resonance technique, involving two resonant power buildup cavities (BUCs) in series. Inside the first BUC, the analyte molecules are pumped to the  $v=2$  manifold by  $cw$  interaction with  $1.5\text{ }\mu\text{m}$  radiation from a Burleigh FCL-220 color center laser. After traversing the first BUC, molecules enter the second BUC where they are further excited to the  $v=6$  level by  $0.8\text{ }\mu\text{m}$  radiation from a Microlase (now Coherent/Scotland) MBR-110 Ti:sapphire laser. Upon exiting the second BUC, the molecular beam enters the bolometer housing through a 1 mm wide vertical slit, and impacts a composite silicon bolometer (Infrared Labs unit 657). The bolometer is cooled to  $\sim 1.6\text{ K}$  by pumping on its liquid helium reservoir. Phase sensitive detection is performed by amplitude modulating the  $0.8\text{ }\mu\text{m}$  laser and lock-in detecting the bolometer signal.

Absolute frequency reference is provided by a home-built wavemeter, which is known to have a systematic error of approximately  $0.02\text{ cm}^{-1}$ . This error is likely due to the dispersion of air, which is calculated to lead to a correction of about  $0.017\text{ cm}^{-1}$  in this wavelength region. Relative frequency calibration is supplied by monitoring a hermetically sealed, temperature stabilized 750 MHz confocal scanning etalon, which has a residual drift of about 30 MHz/hour.

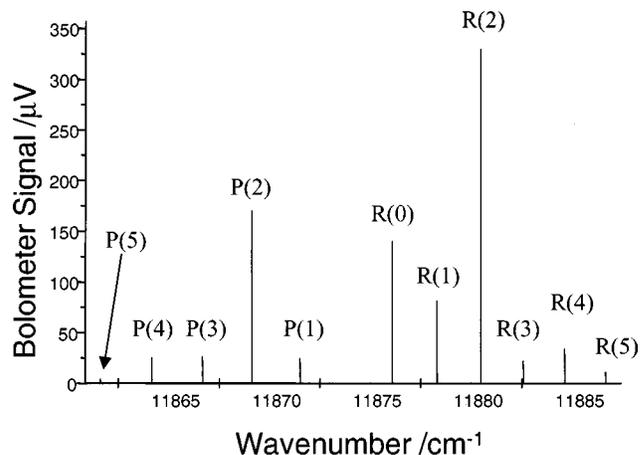


FIG. 1. Stick spectrum of observed lines in the  $006^+$  spectrum of  $^{12}\text{C}_2\text{H}_2$ . The horizontal axis is the photon energy of the  $6\leftarrow 2$  step.

We performed experiments on both  $^{12}\text{C}_2\text{H}_2$  and  $^{13}\text{C}_2\text{H}_2$ . The normal acetylene was purchased from Matheson, and used without further purification. It was diluted to a concentration of 1% in helium, and expanded at a stagnation pressure of 8 bar. The  $^{13}\text{C}$ -labeled acetylene was purchased from Icon Services Inc. with a stated 99% atom purity, and was used without further purification. The sample was diluted to a 0.65% mixture in He, and expanded at a stagnation pressure of 4 bar. The lower concentration and backing pressure for the  $^{13}\text{C}_2\text{H}_2$  spectra was necessitated by a desire to maximize the scanning time from this expensive sample.

## $^{12}\text{C}_2\text{H}_2$ RESULTS—SPECTRAL ANALYSIS

An experimental stick “spectrum” of the  $006^+$  level of  $^{12}\text{C}_2\text{H}_2$  is shown in Fig. 1. The  $x$ -axis shows the photon energy of the  $6\leftarrow 2$  step, and the labels on the lines follow the traditional nomenclature, with the “ground” state being the  $v=2$  level. The spectrum is a little more interesting than Fig. 1 suggests, however, as both the  $J'=2$  and  $J'=4$  levels are split into two components, while no other observed levels (including the  $J'=0$  and 6 levels) are found to be split. The term value of each  $J$ -level in the  $v=6$  manifold is shown in Table I, and is the sum of the wave numbers of the two photons, plus the rotational term value of the ground state molecules. (The ground state rotational constants have been taken from Ref. 13) For the levels which are split, the center of gravity of the two peaks is reported.

TABLE I. Rotational energy levels for the  $006^+$  vibrational level of  $^{12}\text{C}_2\text{H}_2$ . The values for  $J=2$  and 4 are the intensity weighted centers of gravity of the pairs of perturbed levels.

$J$	Energy ( $\text{cm}^{-1}$ )
0	18 430.289
1	18 432.557
2	18 437.101
3	18 443.913
4	18 453.009
5	18 464.342
6	18 477.994

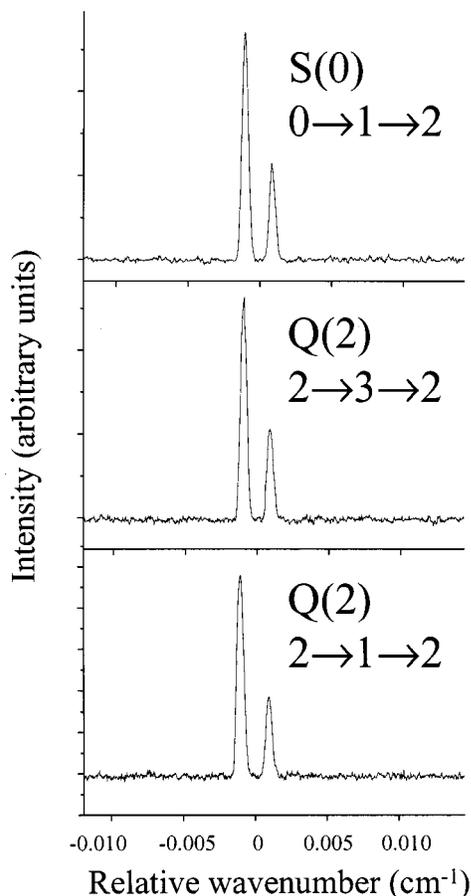


FIG. 2. Spectra of three different transitions that terminate at the  $J' = 2$  level in the  $006^+$  level of  $^{12}\text{C}_2\text{H}_2$ . The splitting of the two peaks is 60 MHz.

Some of the upper levels in the spectrum shown in Fig. 1 were observed using more than one transition. Owing to the nature of a double resonance spectrum, it is possible to record most  $J$ -levels in multiple ways. Since the end result is a transition to the same  $J$ -level in the  $\nu = 6$  state, the different spectra should look identical. For example, Fig. 2 shows the three spectra that have  $\nu = 6$ ,  $J' = 2$  as the final state. If we adopt a nomenclature where we use the traditional  $P$ ,  $Q$ ,  $R$  labels for each step of the process, listing the  $2 \leftarrow 0$  transition first, we see that Fig. 2 shows from top to bottom the  $R(0)R(1)$ ,  $R(2)P(3)$ , and  $P(2)R(1)$  transitions. These resonant two photon transitions correspond to the  $S(0)$ ,  $Q(2)$ , and  $Q(2)$  transitions, respectively. It is important to note that the same splitting (60 MHz) and intensity ratio (2.4:1) is observed in all spectra, which provides an internal consistency check and demonstrates nicely the reproducibility and reliability of the spectrometer.

The splitting of a level into two components is a classic case of a zeroth-order bright state being perturbed by a near resonant dark state. The interaction between the two levels results in a pair of mixed eigenstates, both of which are observed experimentally. From the line positions and relative intensities, it is possible to deperturb the spectrum and obtain the positions of the bright and perturbing state, as well as the off-diagonal matrix element between them. A similar phenomenon has been observed for the  $J' = 4$  level as well, but in this case, the splitting is an order-of-magnitude larger (600

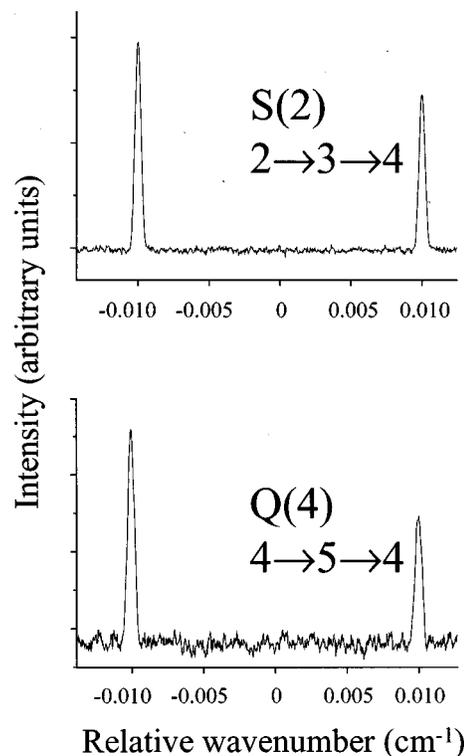


FIG. 3. Spectra of two transitions that terminate at the  $J' = 4$  level in the  $006^+$  level of  $^{12}\text{C}_2\text{H}_2$ . The splitting of the two peaks is 600 MHz.

MHz versus 60 MHz). Figure 3 shows the  $R(2)R(3)$  and  $R(4)P(5)$  transitions, which correspond to  $S(2)$  and  $Q(4)$  transitions, respectively. Note that, due to the rotational cooling present in a molecular beam, there are fewer molecules in the  $J'' = 4$  level, and the signal-to-noise ratio is not as high as in the previous case.

Table II lists the results of the deperturbation for both the  $J' = 2$  and 4 levels. Comparing the two results, we see that the coupling matrix element for the  $J' = 4$  level is an order-of-magnitude larger than for the  $J' = 2$  level. This indicates that two different perturbing states are responsible for the splitting of the two levels. Moreover, since none of the other observed  $J'$ -levels are split, the perturbing states must tune rapidly into and out of resonance (within a single  $J$ ). Such rapid tuning of perturbing states has been witnessed before for acetylene by Scherer *et al.*<sup>2</sup> in direct overtone studies of the  $006^-$  level—the one-photon local mode counterpart of the  $006^+$  level studied here. That experiment, and all other Doppler limited experiments, are only sensitive to much stronger perturbations than those observable in the present work.

TABLE II. Molecular constants for the two perturbed levels in  $^{12}\text{C}_2\text{H}_2$ .

$J$	Observed levels ( $\text{cm}^{-1}$ )	Bright state ( $\text{cm}^{-1}$ )	Perturbing state ( $\text{cm}^{-1}$ )	Coupling matrix element ( $\times 10^3 \text{ cm}^{-1}$ )
2	18 437.098 18 437.110	18 437.098	18 437.099	0.918
4	18 452.999 18 453.019	18 453.007	18 453.011	9.73

TABLE III. Molecular constants of the  $006^+$  and  $006^-$  vibrational levels. The numbers in parentheses represent  $1\sigma$  error estimates.

	$006^+$ (this work)	$006^-$ (Ref. 2)
$\nu_0$ ( $\text{cm}^{-1}$ )	18 430.284(2)	18 430.066(1)
$B'$ ( $\text{cm}^{-1}$ )	1.136 11(13)	1.136 198(13)

## $^{12}\text{C}_2\text{H}_2$ RESULTS—UPPER STATE CONSTANTS

Table III lists the constants for the  $v=6$  level which were determined by performing a whole band fit of the observed second step data. In effect, this was like performing a single photon fit, in which the “ground” state was the  $v=2$  level. The line positions were fit to the polynomial:

$$\nu(m) = \nu_0 + (2B'' + \Delta B)m + (\Delta B - \Delta D)m^2 - 2(2D'' + \Delta D)m^3 - \Delta Dm^4, \quad (1)$$

where  $\nu_0$  is the band origin,  $B''$  is the rotational constant for the  $v=2$  manifold,  $\Delta B$  is the difference between the  $v=6$  and  $v=2$  rotational constants,  $D''$  is the  $v=2$  distortion constant,  $\Delta D$  is the difference between the  $v=6$  and  $v=2$  distortion constants, and  $m$  is  $-J$  for  $P$ -branch lines and  $J+1$  for  $R$ -branch lines. The values for  $B''$  and  $D''$  were constrained to their literature values,<sup>28</sup> while for the split levels, the deperturbed line positions were used. In addition, the  $\Delta D$  value was constrained to be zero, since otherwise it grew unphysically large.

Since the rotational constants are largely unaffected by (+/-) local mode tunneling symmetry, the  $B'$  value obtained for the  $006^+$  level [1.13611(13)] is expected and observed to be in good agreement with the value given for the  $006^-$  level in Ref. 2 [1.136198(13)]. From Table III, we also see that the energy of the  $006^+$  level is determined to be at 18 430.284(2)  $\text{cm}^{-1}$ . This value is 0.218  $\text{cm}^{-1}$  to the blue of the  $006^-$  band center. Interestingly, the article by Halonen *et al.*<sup>29</sup> predicts the  $006^+$  level to lie 0.15  $\text{cm}^{-1}$  to the red of the  $006^-$  level, which is the order predicted by the local/normal mode correlation diagram.<sup>30</sup> The sign of the observed +/- splitting is a surprising result, since previous work in our lab<sup>31</sup> has measured the  $005^+$  level and found it to be shifted 0.62  $\text{cm}^{-1}$  to the blue of the  $005^-$  level, in remarkably good agreement with the prediction by Halonen *et al.* of a local mode shift of 0.63  $\text{cm}^{-1}$  to the blue. In analogy with a previous study of torsional tunneling splittings in vibrational modes of propene,<sup>32</sup> the discrepancy in the order of the local mode doublets in acetylene is likely due to weak perturbations by bath states that have large local mode splittings.

## $^{12}\text{C}_2\text{H}_2$ RESULTS—DENSITY OF STATES ANALYSIS

A formula for estimating the coupled density of states from a spectrum, accounting for the finite signal-to-noise ratio of the experiment has been proposed previously.<sup>33</sup> It reads,

$$\rho_{\text{coupled}} = \frac{\sum (V_i)^{-1}}{2N_B \sqrt{S/N}}, \quad (2)$$

where  $V_i$  is the coupling matrix element of the  $i$ th multiplet,  $N_B$  is the number of observed bright states, and  $S/N$  is the average signal to noise ratio. Using the coupling matrix elements determined from the deperturbation, and an average signal-to-noise ratio of 500 over the entire spectrum, the above formula yields a coupled density of states of roughly 3.8 per  $\text{cm}^{-1}$ . However, given the small number of transitions and perturbations, considerable statistical fluctuations are expected.

The density of states at the energy explored in the present experiment can also be calculated via an anharmonic direct count method, using the molecular constants of Ref. 13. The total anharmonic density of  $\Sigma$  vibrational states was calculated to be approximately 3.5 states per  $\text{cm}^{-1}$  (averaged over a 100  $\text{cm}^{-1}$  wide interval centered at 18 430  $\text{cm}^{-1}$ ), which, when divided by 4 (a factor of two each for parity and  $g/u$  symmetries) yields a density of  $\Sigma_g^+$  vibrational states of less than 1 state per  $\text{cm}^{-1}$ . Since this is a  $\Sigma \rightarrow \Sigma$  transition, the  $l$  quantum number is zero in both the upper and lower states. Therefore, in the anharmonic approximation we can only couple states that have  $l=0$ . Coriolis coupling, however, can mix states with  $l \leq J$ , and a complete breakdown of  $l$  symmetry will result in a density of states that is  $(2J+1)$  times higher than the anharmonic count. Given the low  $J$ -states observed here, the maximum possible density of states is less than 10 per  $\text{cm}^{-1}$ .

It is worth pointing out that the density of vibrational states reported in Ref. 2 (which was based upon the Whitten–Rabinovitch expression)<sup>34</sup> is the total and not the symmetry accessible density of vibrational states. In general, for two states to couple by anharmonic interaction, they must be close in energy, have the same  $J$ -value, be of the same parity and symmetry with respect to exchange of identical nuclei, and have the same  $l$  quantum number. In particular, for the  $\Sigma$  states reported here, care must be taken to only count those states with  $l=0$ , which was not done in Ref. 2. When these considerations are taken into account, we conclude that the density of symmetry allowed vibrational states of unique symmetry in highly excited acetylene is significantly lower (by more than a factor of 10) than previously predicted.

## $^{13}\text{C}_2\text{H}_2$ RESULTS—SPECTRAL ANALYSIS

For the  $^{13}\text{C}$  isotope of acetylene, we recorded lines in the  $2131 \text{ } ^1_1^{-1}$  level, where the 1.5  $\mu\text{m}$  laser first deposits molecules in the  $1101 \text{ } ^1_1^{-1}$  state, and the 0.8  $\mu\text{m}$  laser subsequently excites a fraction of them to the  $2131 \text{ } ^1_1^{-1}$  state. We are able to efficiently excite this delocalized ( $1101 \text{ } ^1_1^{-1}$ ) state in this isotopomer because it is in anharmonic resonance with the 10100 state, which carries the dominant transition strength in this spectral region. A total of four rotational transitions which terminate in this level were observed. Figure 4 shows a spectrum of the  $R(2)R(3)$  transition, and as in the case of the  $^{12}\text{C}_2\text{H}_2$   $J'=4$  level, we see that it is split into two components. However, unlike the  $^{12}\text{C}_2\text{H}_2$  spectrum, three of the four observed transitions of the C-13 isotope are split ( $J'=1, 3$  and  $4$ ). The  $J'=2$  level may also be split, but we were unable to get the Ti:Al<sub>2</sub>O<sub>3</sub> laser to scan continuously in the region surrounding the observed

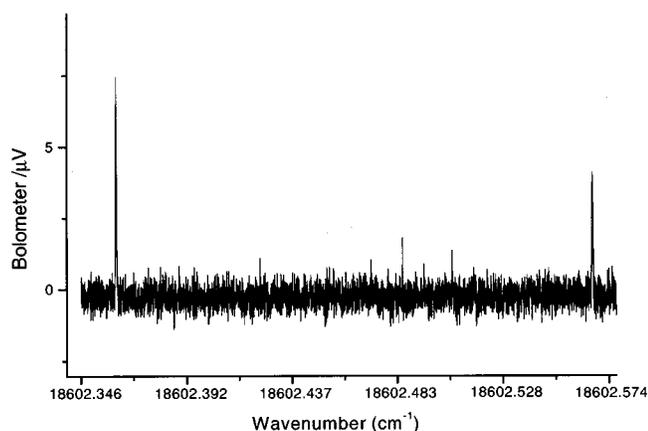


FIG. 4. Spectrum of the  $R(2)R(3)$  transition in the  $2131\ 1^{-1}$   $\leftarrow 1101\ 1^{-1}$  band of  $^{13}\text{C}_2\text{H}_2$ .

$J'=2$  transition. Table IV lists the line positions for each observed transition of  $^{13}\text{C}_2\text{H}_2$ , as well as the results of the deperturbation procedure for each.

The splittings that we observed in  $^{13}\text{C}_2\text{H}_2$  were much larger than those in  $^{12}\text{C}_2\text{H}_2$ , ranging from 3.6 to 6 GHz. Consequently, the coupling matrix elements were significantly larger for  $^{13}\text{C}_2\text{H}_2$ , as a comparison of Tables IV and II reveals. In essence, the pure CH stretch level of  $^{12}\text{C}_2\text{H}_2$  (an extreme motion state) has enhanced stability with respect to a combination state. This behavior has been seen in acetylene before, as the  $005^-$  and  $006^-$  CH stretch overtone spectra of acetylene show only weak perturbations.<sup>2</sup> In contrast, the spectra observed in the same energy region by stimulated emission pumping, which puts energy in both the *trans* bending mode and the CC stretching mode, are much more highly perturbed.<sup>6,7</sup> Also, recent work at MIT has shown that the stimulated emission pumping spectra of acetylene are less perturbed when all of the excitation is deposited into a *trans* bending mode.<sup>8</sup>

Inspection of the intensity data in Table IV reveals that, despite the fact that the  $2131\ 1^{-1}$  level has 1 quantum of excitation in the *trans* CH bending mode, there is no evidence of the 9:1 and 3:3 tunneling splittings that would be indicative of hydrogen exchange isomerization. Moreover, the intensities of the lines, as evidenced by Fig. 4, are weaker than in the  $^{12}\text{C}_2\text{H}_2$  spectra, despite the fact that the first step of the double resonance excitation is saturated. We can explain the low intensity by considering the fact that the first step doesn't provide any effective "anharmonicity enhancement." After the first step (excitation to  $1101\ 1^{-1}$ ), we have no quanta in the  $\nu_3$  mode, into which the second step is

supposed to deposit three quanta of excitation. As a result, the signal level is about what we would expect from a single photon  $\nu_1 + 3\nu_3$  spectrum, with the exception that only half of the intensity is available because the initial excitation has broken the "degeneracy" of the two CH chromophores. In contrast, the transition into the  $4111\ 1^{-1}$  level of  $^{13}\text{C}$  acetylene should be more intense, since the second step would effectively be a  $3\nu_1 + \nu_3$  transition. Since there would be one quantum of excitation in the  $\nu_1$  mode after the first step, depositing three additional quanta in this mode in the second step should be easier than the second excitation step for the  $2131\ 1^{-1}$  level discussed earlier.

In the hope of observing more and stronger lines to improve the statistical analysis of the coupled density of states, we attempted to scan the  $4111\ 1^{-1}$  level. However, despite scanning  $30\ \text{cm}^{-1}$  to the red and  $15\ \text{cm}^{-1}$  to the blue of the expected band center, we failed to detect any lines. Given that the apparatus continued to perform adequately during the search (which was verified by rescanning lines terminating in the  $2131\ 1^{-1}$  level), there are only two explanations for the absence of observed lines. First, the prediction of the band center could be in error. This highly "delocalized" upper state is of quite different vibrational character than the states used to fit the parameters of the model. While we believe that this is the likely cause, we would like to point out that the predicted position for the  $2131\ 1^{-1}$  level deviated by only  $2\ \text{cm}^{-1}$  from the observed value, and there is no reason to expect that the prediction would be significantly worse for the  $4111\ 1^{-1}$  level. Second, the signal might be too weak to be observed, perhaps because of fractionation which would cause the intensities of the resulting eigenstate transitions to be below the detection threshold of the spectrometer. However, the density of states for acetylene is far too low to produce a highly fractionated spectrum, and the oscillator strength of each line in this band should be stronger than those of the transitions into the previously observed  $2131\ 1^{-1}$  level, as mentioned earlier.

### $^{13}\text{C}_2\text{H}_2$ RESULTS—UPPER STATE CONSTANTS

With only four observed rotational lines, deriving meaningful data from a five parameter fit as in Eq. (1) is impossible. Instead, we fit the positions of the four observed lines of  $^{13}\text{C}_2\text{H}_2$  to the simplified expression,

$$\nu(m) = \nu_0 + (B' + B'')m + (B' - B'')m^2, \quad (3)$$

where  $\nu_0$  is the band center,  $B'$  and  $B''$  are the upper and lower ( $\nu = 1101\ 1^{-1}$  here) state rotational constants, respectively, and  $m = -J$  for the *P*-branch and  $J+1$  for the

TABLE IV. Observed and deconvoluted line positions in  $^{13}\text{C}_2\text{H}_2$ .

$J$	Observed levels ( $\text{cm}^{-1}$ )		Intensity ratio	Bright state ( $\text{cm}^{-1}$ )	Perturbing state ( $\text{cm}^{-1}$ )	Coupling matrix element ( $\text{cm}^{-1}$ )
1	18 582.809	18 582.983	0.45:0.55	18 582.904	18 582.888	0.0866
2	18 587.185					
3	18 593.647	18 593.768	0.36:0.64	18 593.724	18 593.691	0.0582
4	18 602.361	18 602.566	0.58:0.42	18 602.447	18 602.481	0.1017

R-branch. The lower state rotational constant was constrained to the value given by Herman *et al.*<sup>14</sup> for the  $1101\ 1^1\ 1^{-1}$  state. From the fit, the vibrational term value,  $G(2131\ 1^1\ 1^{-1})$ , is determined to be  $18\,580.721(31)\ \text{cm}^{-1}$ , and  $B(2131\ 1^1\ 1^{-1})$  is  $1.0867(26)\ \text{cm}^{-1}$ . Calculations of the  $2131\ 1^1\ 1^{-1}$  level using the polyad model<sup>35</sup> yield the  $G(2131\ 1^1\ 1^{-1})$  value to be  $18\,578.365\ \text{cm}^{-1}$  with a  $B$  value of  $1.090\ \text{cm}^{-1}$ .

### $^{13}\text{C}_2\text{H}_2$ RESULTS—DENSITY OF STATES ANALYSIS

The procedure described earlier for  $^{12}\text{C}_2\text{H}_2$  was followed to compute the density of states for  $^{13}\text{C}_2\text{H}_2$  as well. From Eq. (2), and an average  $S/N$  ratio of 10 over the entire observed spectrum, the experimentally observed density of coupled states was computed to be approximately  $1.5\ \text{per}\ \text{cm}^{-1}$ . In comparison, the symmetry allowed density of states from the anharmonic direct count method is  $0.8\ \text{per}\ \text{cm}^{-1}$ , using the constants given in Ref. 14 and counting states in a  $100\ \text{cm}^{-1}$  wide interval centered at  $18\,580\ \text{cm}^{-1}$ .

As pointed out earlier for the  $^{12}\text{C}$ -acetylene, even at  $18\,000\ \text{cm}^{-1}$ , the density of states is very sparse. Moreover, the experimentally observed density of states analysis leads us to believe that, on the long-time scale of this experiment (10 ns), the molecule is accessing the full density of states available to it. This means that, on the timescale of 10 ns, the approximate quantum numbers<sup>36</sup> of the polyad model are not conserved. This observation does not contradict the validity of the polyad quantum numbers on the 1 ps time scale, as inferred from spectra of  $10^4$  times lower resolution.

We would like to discuss our work in light of a recent study of vinylidene by Coulomb explosion imaging,<sup>37</sup> where it was found that  $3.5\ \mu\text{s}$  after production of vinylidene, the population of the vinylidene isomer is still 50%. The framework given by the authors of Ref. 37 is that the vinylidene zeroth-order state interacts with only one or two acetylene basis states. This analysis is consistent with the picture of highly excited acetylene obtained here, but is in apparent contrast to previous theoretical<sup>17,23</sup> and experimental work,<sup>38</sup> in which the vinylidene lifetime is predicted to be on the order of a few picoseconds. We would like to point out that in the semiclassical treatment of Ref. 23, only the time for vinylidene to tunnel through the classical barrier was calculated, and since at the energy of the barrier maximum the acetylene manifold is sparse, recurrences of the initially prepared vinylidene character will occur. That the authors understood this point is evidenced by footnote 22 in their article, but this has not been realized by some other authors who have discussed this work. The work by Schork and Köppel (Ref. 17) used a dynamical wave packet propagation technique on an *ab initio* potential energy surface calculated using coupled-cluster theory at the CCSD(T)/cc-pVTZ level. However, since the deep acetylene wells have not been explicitly included in their calculated potential energy surface, they include a complex absorbing potential (CAP) to irreversibly remove the parts of the wave packet that cross the barrier to isomerization. In essence then, they have simulated the acetylene basis states as a continuum. However, since the acetylene manifold in reality is sparse, the CAP vastly over-

estimates the effects of the acetylene basis states, and thus underestimates the lifetime of vinylidene.

Much of the goal of the previous theoretical studies was to account for the experimental data reported by Ref. 38—in fact, Schork and Köppel reproduce quite nicely the observed photodetachment spectrum of Ervin *et al.* However, the estimation of the vinylidene lifetime, as acknowledged in Ref. 38, is complicated by the low resolution of the experiment. Reference 38 estimates the “lifetime” of the vinylidene isomer by calculating the “excess width” between observed triplet and singlet levels. Since the barrier to triplet vinylidene isomerization is calculated to be very large ( $>50\ \text{kcal/mol}$ ),<sup>39</sup> the triplet transition isn’t expected to be significantly lifetime broadened. However, the singlet vinylidene state is observed to be broader, and the “excess width” between the triplet and singlet lines was attributed to lifetime broadening. Since the observed bands in the photodetachment spectra were not rotationally resolved, it was necessary to specify the rotational temperature of the species in order to define the expected rotational contour for the observed band. To determine the rotational temperature, Ervin *et al.* simulated the temperature of the triplet transition, and then used this value to fix the temperature of the singlet transition. We would like to point out that the assumption that the singlet and triplet “temperatures” are the same is open to question. The triplet transition is a parallel (*a*-type) transition, whereas the singlet transition is perpendicular (*c*-type). It is well-known<sup>1</sup> that for perpendicular transitions the width of the rotational envelope is affected by the  $K$  temperature, and the  $K$  quantum number typically cools in a supersonic expansion less rapidly than  $J$ . So the “excess width” observed in the singlet photodetachment spectrum could be explained by normal rotational broadening. One indication that the “excess width” is not due to lifetime broadening was presented in Ref. 38. They noted that excitation of two quanta in the CH rock mode, which is believed to be nearly identical to the reaction coordinate, does not produce any noticeable increase in lifetime broadening. This is an important result, as it suggests that the observed broadening is not due to lifetime effects. We would like to acknowledge that while the best estimate of the lifetime of singlet vinylidene was bracketed as  $\tau=0.04\text{--}0.2\ \text{ps}$ , Ervin *et al.* also pointed out that they could not rule out the possibility that the *entire observed width* was a convolution of instrument resolution and rotational contour.

Based upon the observed density of vibrational states of  $\Sigma_g^+$  symmetry, the Coulomb explosion results can be rationalized if the “lifetime” for semiclassical tunneling of vinylidene is on the order of 8 ps. This value is calculated using the following expression:

$$N - 1 = \frac{\rho}{2\pi c \tau},$$

where  $\tau$  is the “lifetime,”  $\rho$  is the density of states, and  $N$  is the number of eigenstates over which the vinylidene character is diluted. This lifetime is a bit longer than the high end of the range predicted by Carrington *et al.*,<sup>23</sup> based upon uncertainties in the barrier height. This estimate is made assuming vinylidene can couple statistically to the full symme-

try allowed density of acetylene levels. Any dynamical constraints (reflecting approximately conserved acetylene vibrational quantum numbers on the time scale of the tunneling), will reduce the effective density,  $\rho$ , and thereby decrease the estimate of the tunneling time,  $\tau$ , proportionally. The conclusion of these considerations is that there is no experimental evidence, including the Coulomb explosion experiment, to suggest that qualitative conclusions of the work of Carrington *et al.* need to be modified.

### LIMITATION ON THE HYDROGEN EXCHANGE ISOMERIZATION RATE

Based upon the lack of observed tunneling splittings, or even increased width of the  $^{13}\text{C}_2\text{H}_2$  transitions, we can put an upper limit of 15 MHz on the tunneling splitting, which implies that the time to tunnel from one acetylene minimum to the other is at least 30 ns. We note that this limit applies not only to the “bright state” observed in the experiment (which has most of its energy in the stretching modes) but also for the two odd  $J$  perturber states. We can rule out the hypothesis that the perturbers have very large tunneling splittings because in that case, three lines should have been observed in the spectrum as only one component of the bright state doublet would have been perturbed and shifted. As discussed above, the density of states analysis suggests that these perturbers are part of an ensemble that includes most of the microcanonical ensemble, i.e., that these are “typical states” at this energy. As such, based upon the classical equipartition theorem, we can predict that on average they have approximately half of their total vibrational energy contained in the bending degrees of freedom (there are three stretching modes and three bending modes once the constraint that  $K=0$  is satisfied).

In order to put a perspective on this upper limit of 30 ns to the tunneling rate, it is useful to compare with the rate predicted by statistical reaction rate theory. We have estimated the RRKM isomerization rate to be  $\sim 1$  ps, using the barrier height and harmonic frequencies at the transition state reported by Ref. 40 (which predicts  $N^\ddagger = 11$ , where  $N^\ddagger$  is the number of vibrational levels of the transition state with appropriate symmetry in the energy window of our experiment), and the density of states  $\rho = 0.8$  cm reported above.

Thus, our upper limit on the rate of isomerization for “typical” states of  $^{13}\text{C}_2\text{H}_2$  approximately  $3000\text{ cm}^{-1}$  above the classical barrier is 30 000 times smaller than the statistical prediction. Similar behavior has also been noted for HOCl,<sup>41</sup> where it was found that the measured unimolecular dissociation rate was three orders-of-magnitude slower than the statistical rate. Since RRKM must give the initial (before possible barrier recrossings) isomerization rate for a microcanonical ensemble,<sup>42</sup> we have the result that the rate for two “typical” states are over four orders-of-magnitude below that for the microcanonical average. Earlier experiments on near threshold dissociation of  $\text{H}_2\text{CO}$  (Ref. 43) and  $\text{NO}_2$  (Ref. 44) have demonstrated eigenstate resolved rates that fluctuate around the RRKM values. Theory predicts that for a strongly mixed quantum system, the distribution of rates should be approximately a  $\chi^2$  distribution with  $N^\ddagger$  degrees of

freedom,<sup>45</sup> which would rule out our present observations as due to “fluctuations”.

The present results suggest that at  $18\,500\text{ cm}^{-1}$  of vibrational excitation in  $^{13}\text{C}_2\text{H}_2$ , there is a strong dynamical bottleneck that separates the phase space that can classically isomerize from the bulk of phase space that cannot. We would like to point out that such a dynamical picture is consistent with the current understanding of acetylene dynamics, which includes a limited number of known anharmonic resonances. It has been found that local bender states, which have excitation nearly along the reaction coordinate for isomerization, are extremely decoupled from the other degrees of freedom and form a quasiperiodic region of phase space.<sup>46</sup>

### SUMMARY

We report, for the first time, spectra and constants of the  $006^+$  level of  $^{12}\text{C}_2\text{H}_2$  and the  $2131\ 1\ 1^{-1}$  level of  $^{13}\text{C}_2\text{H}_2$ . We have found that two rotational levels in the  $006^+$  vibrational level are split by two separate local perturbers, via matrix elements which differ by an order-of-magnitude. The size of these splittings would not be detectable in a Doppler broadened experiment. In a similar fashion, we have found that the  $2131\ 1\ 1^{-1}$  level of  $^{13}\text{C}_2\text{H}_2$  is also affected by local perturbations. A density of states analysis confirms that we are detecting almost the full symmetry-accessible vibrational density of states in our spectra.

An analysis of the relative intensities of the split peaks in the  $2131\ 1\ 1^{-1}$  level of  $^{13}\text{C}_2\text{H}_2$  reveals that the splitting is not due to permutation splittings which are locally large owing to acetylene–vinylidene isomerization. However, the  $^{13}\text{C}_2\text{H}_2$  combination level is observed to be more strongly perturbed than the “pure” CH stretch overtone of  $^{12}\text{C}_2\text{H}_2$ .

We have also addressed a previous ambiguity in the literature about the symmetry accessible vibrational density of states for highly excited acetylene, and attempted to reconcile this result with previous experimental and theoretical work.

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<sup>1</sup>G. Herzberg, *Molecular Spectra and Molecular Structure, Volume II: Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1950).

<sup>2</sup>G. J. Scherer, K. K. Lehmann, and W. Klemperer, *J. Chem. Phys.* **78**, 2817 (1983).

<sup>3</sup>A. Campargue, M. Abbouti Tamsamani, and M. Herman, *Mol. Phys.* **90**, 793 (1997).

<sup>4</sup>S.-F. Yang, L. Biennier, A. Campargue, M. Abbouti Tamsamani, and M. Herman, *Mol. Phys.* **90**, 807 (1997).

<sup>5</sup>A. Campargue, L. Biennier, and M. Herman, *Mol. Phys.* **93**, 457 (1998).

<sup>6</sup>E. Abramson, R. W. Field, D. Imre, K. K. Innes, and J. L. Kinsey, *J. Chem. Phys.* **83**, 453 (1985).

<sup>7</sup>Y. Chen, D. M. Jonas, J. L. Kinsey, and R. W. Field, *J. Chem. Phys.* **91**, 3976 (1989).

- <sup>8</sup>M. P. Jacobson, J. P. O'Brien, R. J. Silbey, and R. W. Field, *J. Chem. Phys.* **109**, 121 (1998).
- <sup>9</sup>M. Abbouti Tamsamani and M. Herman, *J. Chem. Phys.* **102**, 6371 (1995).
- <sup>10</sup>M. Abbouti Tamsamani and M. Herman, *J. Chem. Phys.* **105**, 1355 (1996).
- <sup>11</sup>M. Abbouti Tamsamani, M. Herman, S. A. B. Solina, J. P. O'Brien, and R. W. Field, *J. Chem. Phys.* **105**, 11357 (1996).
- <sup>12</sup>M. Herman, M. I. El Idrissi, A. Pisarchik, A. Campargue, A.-C. Gaillot, L. Biennier, G. Di Lonardo, and L. Fusina, *J. Chem. Phys.* **108**, 1377 (1998).
- <sup>13</sup>M. I. El Idrissi, J. Liévin, A. Campargue, and M. Herman, *J. Chem. Phys.* **110**, 2074 (1999).
- <sup>14</sup>G. Di Lonardo, L. Fusina, E. Venuti, J. W. C. Johns, M. I. El Idrissi, J. Liévin, and M. Herman, *J. Chem. Phys.* **111**, 1008 (1999).
- <sup>15</sup>M. E. Kellman, *J. Chem. Phys.* **93**, 6630 (1990).
- <sup>16</sup>M. E. Kellman and G. Chen, *J. Chem. Phys.* **95**, 8671 (1991).
- <sup>17</sup>R. Schork and H. Köppel, *Theor. Chem. Acc.* **100**, 204 (1998).
- <sup>18</sup>P. S. Skell and J. H. Plonka, *J. Am. Chem. Soc.* **92**, 5620 (1970).
- <sup>19</sup>J. F. Stanton and J. Gauss, *J. Chem. Phys.* **110**, 1831 (1999).
- <sup>20</sup>D. M. Jonas, S. A. B. Solina, B. Rajaram, R. J. Silbey, R. W. Field, K. Yamanouchi, and S. Tsuchiya, *J. Chem. Phys.* **99**, 7350 (1993).
- <sup>21</sup>K. Yamanouchi, N. Ikeda, S. Tsuchiya, D. M. Jonas, J. K. Lundberg, G. W. Adamson, and R. W. Field, *J. Chem. Phys.* **95**, 6330 (1991).
- <sup>22</sup>Y. Q. Chen, S. Halle, D. M. Jonas, J. L. Kinsey, and R. W. Field, *J. Opt. Soc. Am. B* **7**, 1805 (1990).
- <sup>23</sup>T. Carrington, Jr., L. M. Hubbard, H. F. Schaefer III, and W. H. Miller, *J. Chem. Phys.* **80**, 4347 (1984).
- <sup>24</sup>T. C. Germann and W. H. Miller, *J. Chem. Phys.* **109**, 94 (1998).
- <sup>25</sup>J. K. Lundberg, in *Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping*, edited by H.-L. Dai and R. W. Field (World Scientific, Singapore, 1995).
- <sup>26</sup>We adopt the nomenclature used in Ref. 2. For  $^{12}\text{C}_2\text{H}_2$ , we label states according to their local mode quantum numbers  $n, \nu_2, m^\pm$ , where  $\nu_2$  is the CC stretch quantum number,  $m$  quanta of excitation in one local CH stretch, and  $n(\leq m)$  in the other, and the states have been symmetrized (+) or antisymmetrized (-). For  $^{13}\text{C}_2\text{H}_2$ , we use the normal mode quantum numbers  $\nu_1, \nu_2, \nu_3, \nu_4^4, \nu_5^5$ , where  $\nu_1$  and  $\nu_3$  denote the CH stretches (with  $\nu_1 < \nu_3$ ),  $\nu_2$  is the CC stretch quantum number,  $\nu_4$  and  $\nu_5$  are the quantum numbers for the  $\Pi_g$  and  $\Pi_u$  bends, respectively, and  $l_4$  and  $l_5$  are the vibrational angular momentum quantum numbers for those modes.
- <sup>27</sup>H. K. Srivastava, A. Conjusteau, H. Mabuchi, A. Callegari, K. K. Lehmann, and G. Scoles, *Rev. Sci. Instrum.* (in press).
- <sup>28</sup>K. Nakagawa, M. de Labachellerie, Y. Awaji, and M. Kourogi, *J. Opt. Soc. Am. B* **13**, 2708 (1996).
- <sup>29</sup>L. Halonen, M. S. Child, and S. Carter, *Mol. Phys.* **47**, 1097 (1982).
- <sup>30</sup>M. S. Child and L. Halonen, *Adv. Chem. Phys.* **57**, 1 (1984).
- <sup>31</sup>J. E. Gambogi, Ph.D. thesis, Princeton University, 1994.
- <sup>32</sup>A. Ainarschian, G. T. Fraser, J. Ortigoso, and B. H. Pate, *J. Chem. Phys.* **100**, 729 (1994).
- <sup>33</sup>A. McIlroy, D. J. Nesbitt, E. R. Th. Kerstel, B. H. Pate, K. K. Lehmann, and G. Scoles, *J. Chem. Phys.* **100**, 2596 (1994).
- <sup>34</sup>G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.* **38**, 2466 (1963); **41**, 1883 (1964).
- <sup>35</sup>M. P. Jacobsen, Ph.D. thesis, Massachusetts Institute of Technology, 1999.
- <sup>36</sup>The three polyad quantum numbers proposed in Ref. 16 are  $\nu_{\text{stretch}} = \nu_1 + \nu_2 + \nu_3$ ;  $\nu_{\text{resonance}} = 5\nu_1 + 3\nu_2 + 5\nu_3 + \nu_4 + \nu_5$ ;  $l_{\text{total}} = l_4 + l_5$ .
- <sup>37</sup>J. Levin, H. Feldman, A. Baer, D. Ben-Hamu, O. Heber, D. Zajfman, and Z. Vager, *Phys. Rev. Lett.* **81**, 3347 (1998).
- <sup>38</sup>K. M. Ervin, J. Ho, and W. C. Lineberger, *J. Chem. Phys.* **91**, 5974 (1989).
- <sup>39</sup>M. P. Conrad and H. F. Schaefer III, *J. Am. Chem. Soc.* **100**, 7820 (1978).
- <sup>40</sup>N. Chang, M. Shen, and C. Yu, *J. Chem. Phys.* **106**, 3237 (1997).
- <sup>41</sup>A. Callegari, J. Rebstein, R. Jost, and T. R. Rizzo, *J. Chem. Phys.* **111**, 7359 (1999).
- <sup>42</sup>T. Baer and W. L. Hase, *Unimolecular Reaction Dynamics: Theory and Experiments* (Oxford University Press, New York, 1996).
- <sup>43</sup>W. F. Polik, D. R. Guyer, and C. B. Moore, *J. Chem. Phys.* **92**, 3453 (1990).
- <sup>44</sup>J. Miyawaki, K. Yamanouchi, and S. Tsuchiya, *J. Chem. Phys.* **99**, 254 (1993).
- <sup>45</sup>W. H. Miller, R. Hernandez, and C. B. Moore, *J. Chem. Phys.* **93**, 5657 (1990).
- <sup>46</sup>M. P. Jacobson and R. W. Field, *J. Phys. Chem. A* **104**, 3073 (2000).