

Cis-trans isomerization in the S_1 state of acetylene: Identification of cis-well vibrational levels

Anthony J. Merer,^{1,2} Adam H. Steeves,^{3,4} Joshua H. Baraban,³ Hans A. Bechtel,^{3,5} and Robert W. Field^{3,a)}

¹*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*

²*Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada*

³*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

⁴*Department of Pharmaceutical Chemistry, University of California at San Francisco, San Francisco, California 94143, USA*

⁵*Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8226, USA*

(Received 4 March 2011; accepted 19 May 2011; published online 29 June 2011)

A systematic analysis of the S_1 -trans (\tilde{A}^1A_u) state of acetylene, using IR-UV double resonance along with one-photon fluorescence excitation spectra, has allowed assignment of at least part of every single vibrational state or polyad up to a vibrational energy of 4200 cm^{-1} . Four observed vibrational levels remain unassigned, for which no place can be found in the level structure of the trans-well. The most prominent of these lies at $46\,175\text{ cm}^{-1}$. Its ^{13}C isotope shift, exceptionally long radiative lifetime, unexpected rotational selection rules, and lack of significant Zeeman effect, combined with the fact that no other singlet electronic states are expected at this energy, indicate that it is a vibrational level of the S_1 -cis isomer (\tilde{A}^1A_2). Guided by *ab initio* calculations [J. H. Baraban, A. R. Beck, A. H. Steeves, J. F. Stanton, and R. W. Field, *J. Chem. Phys.* **134**, 244311 (2011)] of the cis-well vibrational frequencies, the vibrational assignments of these four levels can be established from their vibrational symmetries together with the ^{13}C isotope shift of the $46\,175\text{ cm}^{-1}$ level (assigned here as cis- 3^16^1). The S_1 -cis zero-point level is deduced to lie near $44\,900\text{ cm}^{-1}$, and the ν_6 vibrational frequency of the S_1 -cis well is found to be roughly 565 cm^{-1} ; these values are in remarkably good agreement with the results of recent *ab initio* calculations. The $46\,175\text{ cm}^{-1}$ vibrational level is found to have a 3.9 cm^{-1} staggering of its K-rotational structure as a result of quantum mechanical tunneling through the isomerization barrier. Such tunneling does not give rise to ammonia-type inversion doubling, because the cis and trans isomers are not equivalent; instead the odd-K rotational levels of a given vibrational level are systematically shifted relative to the even-K rotational levels, leading to a staggering of the K-structure. These various observations represent the first definite assignment of an isomer of acetylene that was previously thought to be unobservable, as well as the first high resolution spectroscopic results describing cis-trans isomerization. © 2011 American Institute of Physics. [doi:10.1063/1.3599091]

I. INTRODUCTION

The concept of cis-trans (geometric) isomerism in certain organic compounds was first recognized by van 't Hoff in 1874.¹ Isomers of this type differ only in the arrangement of the substituents at a carbon-carbon double bond, but do not interconvert because the potential energy barrier to internal rotation about the double bond is far too high to be surmounted at ordinary temperatures. In some cases the cis and trans isomers have very different properties. The classic example¹⁻³ is the pair of butenedioic acids, maleic acid and fumaric acid. In the cis isomer (maleic acid) internal hydrogen bonding can occur between the two carboxylic acid groups, whereas in the trans isomer the hydrogen bonding must occur between adjacent molecules, leading to a much higher melting point. In quantum terms these molecules represent two minima at different

energies on the same potential energy surface, separated by a large potential barrier.

Low lying vibrational levels of the two isomers will have energy level patterns that are characteristic of rigid molecules, though their vibrational frequencies will differ to some extent. Near the isomerization barrier the vibrational structures of the two isomers must merge into a single large amplitude pattern since the vibrational motion must encompass both isomeric forms. Exactly how the vibrational level structure evolves in this non-symmetric double minimum situation has not been fully established, though the basic ideas follow from the many studies that have been made of simpler, symmetric potential barrier situations such as internal rotation⁴ and ammonia-type inversion.⁵⁻⁹

One of the simplest systems that possesses cis and trans isomers is the first excited singlet electronic state (S_1) of acetylene, C_2H_2 . *Ab initio* calculations¹⁰⁻²⁰ predict that the trans isomer is more stable, with the cis isomer lying about 2700 cm^{-1} higher, and the barrier to isomerization (saddle

^{a)} Author to whom correspondence should be addressed. Electronic mail: rffield@mit.edu. Tel.: (617) 253-1489. FAX: (617) 253-7030.

point) about 2000 cm^{-1} higher still. Transitions from the $^1\Sigma_g^+$ ground electronic state to levels of the cis-well are forbidden by the electric dipole selection rules, being $^1A_2-^1A_1$ in the C_{2v} point group. On the other hand, transitions to levels of the trans-well are dipole-allowed ($^1A_u-^1A_g$ in the C_{2h} point group), and their analysis provided one of the first examples of a molecule changing its point group on electronic excitation.^{21–23} Acetylene is light enough that the vibrational structure of the trans-well^{24–26} is not impossibly dense at the energy of the isomerization barrier, which makes it possible to recognize and interpret irregularities that encode the isomerism. Furthermore, there is the possibility that cis-well levels can tunnel through the barrier, pick up some intensity by interaction with nearby trans-well levels, and appear weakly in the absorption spectrum.

The analyses of Refs. 21–26 characterized the Franck-Condon allowed levels of the 1A_u upper state, assigning them to progressions in the ν_2 (C=C stretch) and ν_3 (trans-bend) vibrations. The *ungerade* fundamentals, ν_4 (torsion), ν_5 (C-H antisymmetric stretch), and ν_6 (cis-bend), were established later by analysis of IR-UV double resonance spectra.^{27,28} More recently, jet-cooled excitation spectra²⁹ have revealed a number of new combination levels involving the low-lying bending vibrations, ν_4 and ν_6 . The energies of these new levels could not be explained easily in terms of the known fundamental frequencies. To clarify the assignments of these levels we undertook a systematic analysis of the level structure of the 1A_u (S_1 -trans) well^{30–33} using IR-UV double resonance and one-photon fluorescence excitation spectra. The unexpected positions of the new combination levels turned out to result from unusually strong Darling-Dennison resonance between the ν_4 and ν_6 vibrations.^{30,32} In the end, a very complete picture of the energy level pattern emerged. Together with the data from other workers,^{21–28} some part of every vibrational polyad (or isolated vibrational level which is not part of a polyad) predicted up to a vibrational energy of 4200 cm^{-1} has now been securely identified.

Four observed vibrational levels, for which there was no place in the level structure of the S_1 -trans well,³² remained unassigned in the energy range up to 4200 cm^{-1} . These levels lie at 45 610, 45 735, 46 114, and 46 175 cm^{-1} . For the level at 46 175 cm^{-1} (3977 cm^{-1} above the trans-well origin), the evidence is now clear that it belongs to the cis-well; this level forms the main subject of this paper. The evidence is less complete for the other three vibrational levels but, *taken as a whole*, the evidence for all four levels adds up to a consistent picture.

II. EXPERIMENTAL DETAILS

The spectra of $^{12}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{13}\text{CH}_2$ used for this paper are the same as those reported in Refs. 30–32. Full details were given in Ref. 30, so that only a brief summary is needed here.

Laser-induced fluorescence excitation spectra of pure acetylene were recorded using an unskimmed free jet expansion from a General Valve series 9 pulsed valve, with 0.5 mm orifice diameter and $\sim 200\text{ kPa}$ backing pressure. A Lambda

Physik 3002E pulsed dye laser, frequency-doubled in a β -barium borate crystal, provided the laser radiation, and the fluorescence was detected by a Hamamatsu R331 photomultiplier.¹³⁰ Te_2 vapor was used for frequency calibration.³⁴

For the IR-UV double resonance experiments, infrared radiation was obtained by difference frequency generation in a LiNbO_3 crystal: an injection-seeded Nd:YAG laser (Spectra-Physics PRO-270), operating at 1064 nm, and a tunable dye laser (Lambda-Physik FL2002), operating in the range 740–790 nm, provided the pumping. The IR output was amplified in a second LiNbO_3 crystal to about 3 mJ/pulse. The observed acetylene line widths are about 0.09 cm^{-1} .

Laser excitation spectra of $^{13}\text{C}_2\text{H}_2$ in the region near $46\,200\text{ cm}^{-1}$ were recorded in a static room-temperature cell. The output of a Lambda-Physik FL2002 dye laser, pumped by an XeCl excimer laser, and operating with Coumarin 440 and 450 dyes, was frequency-doubled in a β -barium borate crystal. The sample of $^{13}\text{C}_2\text{H}_2$ (MSD isotopes, 98% enriched) was subjected to several freeze-pump-thaw cycles for further purification, and its fluorescence was recorded by a Hamamatsu R331 photomultiplier. Calibration was again provided by $^{130}\text{Te}_2$ vapor.³⁴

III. BACKGROUND AND DISCOVERY OF THE $46\,175\text{ cm}^{-1}$ VIBRATIONAL STATE

The S_1 -trans well has its zero-point level at $42\,197.57\text{ cm}^{-1}$.²⁴ Its vibrational assignments are simple to make at low energy, but by $46\,000\text{ cm}^{-1}$ the density of the level structure is at the point where the assignments of the weaker bands are not always obvious, for various reasons. At low vibrational energy the fact that the low-lying bending vibrations, ν_4 and ν_6 , have almost the same frequency (764.9 and 768.3 cm^{-1} , respectively²⁷) causes the vibrational structure to form polyads, in each of which the sum of the ν_4 and ν_6 quantum numbers is constant. However, the overtones of the ν_4 and ν_6 modes suffer from strong Darling-Dennison resonance,³⁰ which causes the energy range of each vibrational polyad to expand vastly as the vibrational quantum numbers increase. For example, the $K' = 1$ levels of the $\nu_4 + \nu_6 = 5$ pure-bending polyad (which we abbreviate as B^5) are spread out over 400 cm^{-1} . The combination levels formed by the bending vibrations and the totally symmetric vibrations form similar polyads. There is often considerable overlap between the various polyads and because anharmonic resonances can occur between them³² the structure becomes increasingly complicated. A further problem is created by the half-linear structure of the molecule at the cis-trans isomerization barrier.¹⁴ In such a half-linear structure, one end of the molecule has a CCH bond angle of about 120° while the CCH group at the other end is nearly linear. The minimum energy pathway to isomerization does not lie along any one of the vibrational normal coordinates, but rather along a combination of two coordinates, Q_3 (trans-bend) and Q_6 (cis-bend). The result is huge diagonal cross-anharmonicity (x_{36}) in levels where both ν_3 and ν_6 are excited,^{32,35} which causes the energy spread of the vibrational polyads to increase even more. A final problem is that, because of poor $\tilde{A} - \tilde{X}$ Franck-Condon

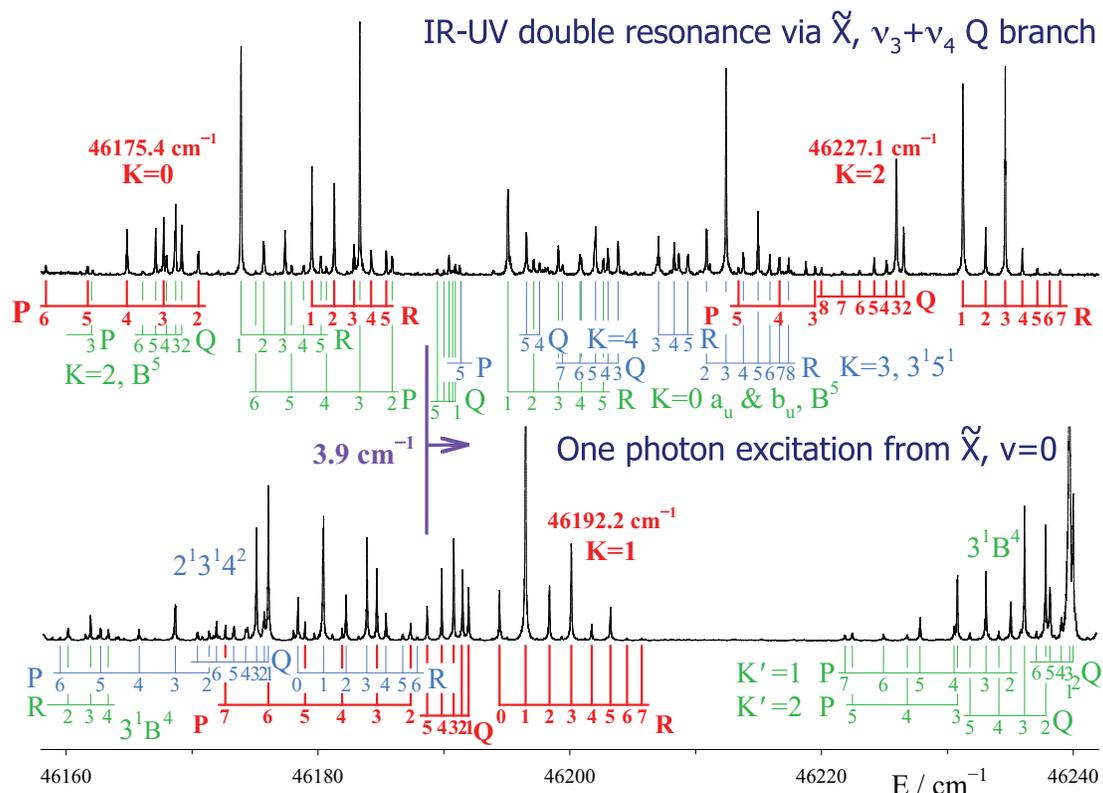


FIG. 1. Upper trace: IR-UV double resonance spectrum of acetylene in the region 46 160–46 240 cm^{-1} recorded via the Q branch of the $\nu_3 + \nu_4''$ band. Two sub-bands, with $K' = 0$ and 2, which cannot be fitted into the manifold of the S_1 -trans state, occur at 46 175.4 and 46 227.1 cm^{-1} . Lower trace: One-photon excitation spectrum of acetylene in the same wavenumber range. A $K' = 1$ sub-band at 46 192.2 cm^{-1} lies 3.9 cm^{-1} above the expected position of the $K' = 1$ sub-band of the upper trace. In both spectra the assignments of the underlying trans-well rotational structure are shown in blue and green.

factors and \tilde{A} -state predissociation effects, some of the expected vibrational bands at higher energy are unobservably weak, which prevents complete sampling of the vibrational manifold.

Both the IR-UV double resonance and the one-photon fluorescence excitation spectra reach this point of complexity at an excitation energy of about 46 000 cm^{-1} . The IR-UV double resonance spectrum is particularly challenging because 15 significantly interacting vibrational levels are expected to lie in the region 45 800–46 200 cm^{-1} . We have invested considerable effort (as yet unpublished) into assigning the states in this region and find that the $K' = 0$ –2 levels of all 15 vibrational levels should lie below 46 150 cm^{-1} with the exception of some of the components of the B^5 polyad. The double resonance spectrum in the region 46 160–46 240 cm^{-1} , as recorded via the Q branch of the infra-red $\nu_3 + \nu_4''$ combination band at 3897 cm^{-1} , is shown in the top part of Fig. 1. The structure of the B^5 polyad can be predicted accurately ($\pm 2 \text{ cm}^{-1}$) from calculations based on the lower energy bending polyads.³⁰ Three of its sub-bands can be assigned at once from the calculations, and two unrelated Coriolis-induced sub-bands, with $K' = 3$ and 4, can also be recognized. This leaves two moderately strong low- K sub-bands unassigned, a $K' = 0$ sub-band at 46 175.4 cm^{-1} and a $K' = 2$ sub-band at 46 227.1 cm^{-1} . Assuming that their upper states belong to the same vibrational level, and recalling that the K -structure of an asymmetric top is described by the energy level expression $[A - 1/2(B + C)]K^2$, their

separation gives the rotational constant $A - 1/2(B + C) = 12.94 \text{ cm}^{-1}$, which is a typical value for the vibrational levels of the S_1 -trans well. Nevertheless, there is no place for these levels in the vibrational manifold of the S_1 -trans well, since every level expected in this region is accounted for. (As we show below, this value of $A - 1/2(B + C)$ is also consistent with a level of the S_1 -cis well.)

The one-photon fluorescence excitation spectrum in the same wavenumber region is illustrated in the lower part of Fig. 1. Most of the bands near this region come from the severely overlapped $2^1 3^1 B^2$ and $3^1 B^4$ polyads. Detailed calculations based on vibrational parameters obtained in fits of lower energy polyads, which take the Coriolis and Darling-Dennison interactions into account, have led to unambiguous assignments for the components of these two polyads.³² All of the observed bands are now accounted for except for a moderately strong $K' = 1$ sub-band at 46 192.2 cm^{-1} . As Fig. 1 shows, this band lies 3.9 cm^{-1} from the position that would be expected for it on the assumption that it belongs to the same vibrational state as the unassigned levels of the double resonance spectrum. However, such an assumption violates the g - u symmetry selection rules if the vibrational state involved is localized in the S_1 -trans well ($\tilde{A}^1 A_u$). Upper states reached in one-photon excitation from the Σ_g^+ ground vibrational level must have *gerade* vibrational symmetry, while upper states reached in double resonance via the $\nu_3 + \nu_4''$ level (which has Π_u symmetry) must be vibrationally *ungerade*. Rotational levels with different values of K in the same

vibrational state cannot have different g - u symmetry. The conclusion is either that the $K' = 1$ level does not belong to the same vibrational state as the $K' = 0$ and 2 levels or that it is not localized in the S_1 -trans well. As we show in Sec. IV, the second alternative is the correct one.

This section has concentrated exclusively on the 46 175 cm^{-1} vibrational level where, as we shall see, the evidence is very strong that this level belongs to the S_1 -cis well. Similar accounts can be given for the 45 610, 45 735, and 46 114 cm^{-1} levels, though the data are not as complete. Those levels are discussed in Sec. V.

IV. ASSIGNMENT OF THE 46 175 cm^{-1} STATE TO THE S_1 -cis ELECTRONIC STATE

A. ^{13}C isotope shifts

Several lines of evidence, in addition to the fact that there is no place for them in the manifold of the S_1 -trans well, indicate that the unassigned levels of Fig. 1 belong to the S_1 -cis well. The strongest argument is based on the carbon isotope shifts of the $K' = 1$ level at 46 192.2 cm^{-1} , which are illustrated in Fig. 2.

Figure 2 contains two spectra, both covering the region 46 184.5–46 210 cm^{-1} . The upper trace is the spectrum of jet-cooled acetylene, where most of the features are due to $^{12}\text{C}_2\text{H}_2$, though some very weak lines of $\text{H}^{12}\text{C}^{13}\text{CH}$, present in natural abundance, also appear. The lower trace is the excitation spectrum of $^{13}\text{C}_2\text{H}_2$, recorded at room temperature in a static cell. The strong saturated lines in this spectrum are high- J lines from the tail of the very intense 3^4_0 , $K = 1-0$ band at 46 260 cm^{-1} ; some of the line assignments are marked at the bottom of the figure. The tie-lines located between the two traces display the rotational assignments of

TABLE I. $^{12}\text{C}_2\text{H}_2$ – $\text{H}^{13}\text{C}^{12}\text{CH}$ isotopomer shifts-per-quantum for the trans-well vibrations of the S_1 state of acetylene, calculated *ab initio* (Ref. 36) for harmonic vibrations. Values are in cm^{-1} . The frequencies given in the left column are the observed fundamentals of S_1 -trans $^{12}\text{C}_2\text{H}_2$.

Vibration	$\Delta\nu$ ($^{12}\text{C}_2\text{H}_2 - \text{H}^{13}\text{C}^{12}\text{CH}$)
ν_1 (a_g , 2880.1 cm^{-1})	4.0
ν_2 (a_g , 1386.9)	25.9
ν_3 (a_g , 1047.6)	6.2
ν_4 (a_u , 764.9)	1.1
ν_5 (b_u , 2857.5)	5.5
ν_6 (b_u , 768.3)	1.2

the $K' = 1$ band at 46 192 cm^{-1} ($^{12}\text{C}_2\text{H}_2$) and the corresponding bands of $\text{H}^{12}\text{C}^{13}\text{CH}$ and $^{13}\text{C}_2\text{H}_2$. It is immediately clear that the isotope shift for $^{13}\text{C}_2\text{H}_2$ is almost exactly twice that for $\text{H}^{12}\text{C}^{13}\text{CH}$, confirming that the bands of all three isotopomers have the same vibrational assignment; also that the bands shift to higher frequency with increasing ^{13}C substitution. The actual isotope shifts are $\Delta\nu$ ($^{12}\text{C}_2\text{H}_2 - \text{H}^{12}\text{C}^{13}\text{CH}$) = -3.03 cm^{-1} and $\Delta\nu$ ($^{12}\text{C}_2\text{H}_2 - ^{13}\text{C}_2\text{H}_2$) = -6.13 cm^{-1} .

The $^{12}\text{C}_2\text{H}_2$ – $\text{H}^{12}\text{C}^{13}\text{CH}$ isotope shifts for the trans-well vibrations ν_1 – ν_4 were determined in Ref. 32, where the shifts per quantum were given as ν_1 : 3.8 cm^{-1} ; ν_2 : 23.4 cm^{-1} ; ν_3 : 5.3 cm^{-1} ; and ν_4 : 0.9 cm^{-1} . (The shifts for ν_5 and ν_6 should be similar to those of ν_1 and ν_4 , as can be seen from the results of recent *ab initio* calculations,³⁶ given in Table I.) The isotope shift of the zero-point level is roughly -6.8 cm^{-1} , which means that the vibrational contribution to the $^{12}\text{C}_2\text{H}_2$ – $\text{H}^{13}\text{C}^{12}\text{CH}$ isotope shift of the 46 192 cm^{-1} band would be about 3.8 cm^{-1} if it belongs to the trans-well. The upper state of the 46 192 cm^{-1} band must be a combination level if it belongs to the trans-well, since it lies 3980 cm^{-1}

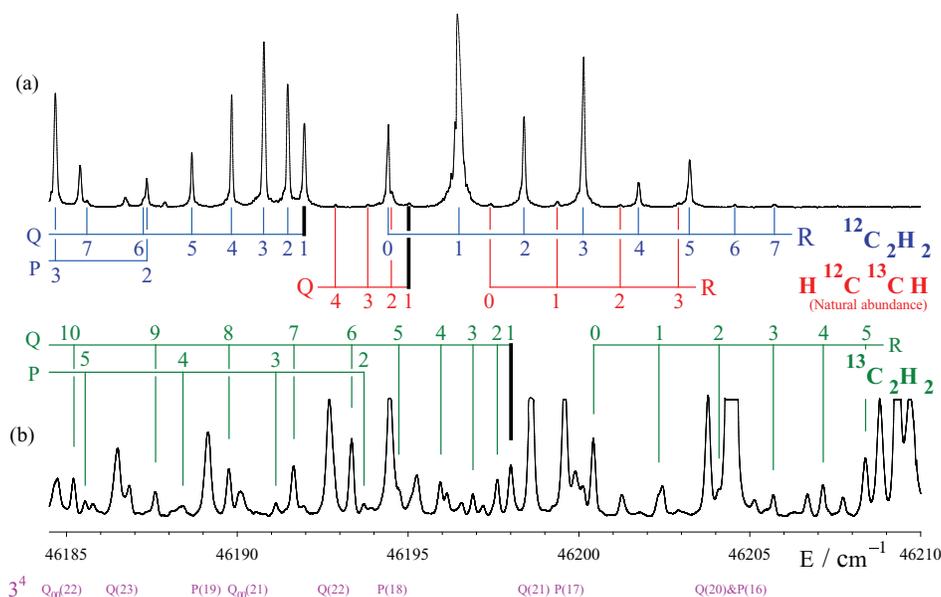


FIG. 2. (a) Jet-cooled excitation spectrum of the 46 192 cm^{-1} ($K' = 1$) sub-band of $^{12}\text{C}_2\text{H}_2$. Some weak lines of $\text{H}^{12}\text{C}^{13}\text{CH}$, present in natural abundance (2%), are also seen. (b) Room temperature excitation spectrum of $^{13}\text{C}_2\text{H}_2$ in the same wavenumber range. The strong lines, which have been artificially truncated, are high- J Q and P lines from the very intense 3^4_0 , $K' = 1$ sub-band at 46 260 cm^{-1} . The assignments of some of them are marked below the wavenumber scale. The tie lines above the spectrum give the assignments of the $^{13}\text{C}_2\text{H}_2$ isotopomer of the 46 192 cm^{-1} band. To make the isotope shifts more visible, the Q(1) tie line has been thickened for the three isotopomers.

TABLE II. Assigned lines of the 46 175 cm⁻¹ band (cis-3¹6¹) and its isotopic counterparts. Values are in cm⁻¹.

J	K = 0 - 1		K = 1 - 0			K = 2 - 1		
	R	P	R	Q	P	R	Q	P
0			46 194.42					
1	46 179.51		46 196.46	46 191.96		46 231.21		
2	46 181.28	46 170.50	46 198.39	46 191.48	46 187.36	46 233.02	46 226.51	
3	46 182.86	46 167.73	46 200.12	46 190.77	46 184.68	46 234.58	46 225.93	46 219.47
4	46 184.21	46 164.81	46 201.74	46 189.83	46 181.92	46 235.94	46 225.14	46 216.65*
5	46 185.41	46 161.71	46 203.23	46 188.67	46 178.97	46 237.13	46 224.18	46 213.39
6		46 158.38	46 204.55	46 187.25		46 238.11	46 223.02	
7			46 205.72	46 185.60		46 238.94	46 221.62	
Isotopic bands, K = 1 - 0								
J	H ¹² C ¹³ CH		¹³ C ₂ H ₂					
	R	Q	R	Q	P			
0	46 197.40		46 200.44					
1	46 199.36	46 195.02	46 202.35	46 198.26				
2	46 201.21	46 194.51	46 204.08	46 197.62	46 193.73			
3	46 202.91	46 193.82	46 205.70	46 196.91	46 191.13			
4	46 204.50*	46 192.87	46 207.14	46 195.95	46 188.41			
5			46 208.38	46 194.75	46 185.55			
6			46 209.69*	46 193.36	46 182.55*			
7			46 210.51	46 191.65	46 179.32			
8			46 211.31	46 189.77	46 175.98			
9			46 211.99	46 187.60	46 172.43			
10			46 212.42	46 185.21	46 168.78			
11			46 212.75*	46 182.55*	46 164.93			
12			46 212.75*	46 179.74	46 160.93			
13				46 176.70*	46 156.76			
14					46 152.30			

*Blended lines are marked with an asterisk.

above the zero-point level. Given the known values of the fundamental frequencies and their isotope shifts, from Table I, it is clear that no trans-well combination level at an energy of 3980 cm⁻¹ can have such a small vibrational contribution to its ¹²C₂H₂-H¹²C¹³CH isotope shift. On the other hand, if the level belongs to the potential well of a different S₁ conformer, for which the minimum lies above that of the trans-well, the vibrational contribution to its isotope shift should be smaller, since the level will lie lower in its potential well. In this context we note that recent *ab initio* calculations³⁶ predict that the zero-point level of the S₁-cis well lies at 44 856 ± 50 cm⁻¹, which is about 2700 cm⁻¹ above the zero-point level of the S₁-trans well. Assuming that the 46 192 cm⁻¹ level belongs to the S₁-cis well, its observed isotope shift matches the expected shift very convincingly, but we defer discussion of it until after the vibrational assignments have been considered (see Sec. V).

The assigned lines of the 46 192 cm⁻¹ band and its isotopomer partners are listed in Table II, along with the lines of the K' = 0-1 and 2-1 sub-bands.

B. Rotational structure of transitions to the S₁-cis well

We have not yet recorded IR-UV double resonance spectra of ¹³C₂H₂ and therefore cannot show from isotope data

alone that the unassigned K' = 0-2 levels of Fig. 1 belong to the same vibrational state, though the lifetime data (see Sec. IV D) strongly suggest that they do. It was noted in Sec. III that, if these three K' levels belong to a single vibrational state of the trans-well, the K' = 1 levels *should not* appear in the one-photon fluorescence excitation spectrum if the K' = 0 and 2 levels appear in the IR-UV double resonance spectrum. However, group theory arguments show that the appearance of the K' = 1 levels in the one-photon spectrum is *precisely what must happen* if the levels belong to a single vibrational state of the cis-well.

It is not necessary to go beyond rigid-molecule considerations to understand the group theory arguments. In essence the difference between the cis and trans isomers is that in C_{2v} symmetry the rovibronic wave functions can transform like all four symmetry species, A₁, A₂, B₁, and B₂, in any given vibronic state, while in C_{2h} symmetry they can only transform as A_g and B_g in a *gerade* vibronic state or A_u and B_u in an *ungerade* vibronic state. Looking up the species of the rotational levels of asymmetric tops in different point groups,³⁷ it is easy to show that the observed R and P branch structure of the K' = 0 sub-band in the double resonance spectra of Fig. 1 will result if the upper state is ^eA₂ × ^vB₂ = ^{ev}B₁ in C_{2v} symmetry or ^eA_u × ^vB_u = ^{ev}B_g in C_{2h} symmetry. Figure 3 is an energy level diagram that shows the branch structures

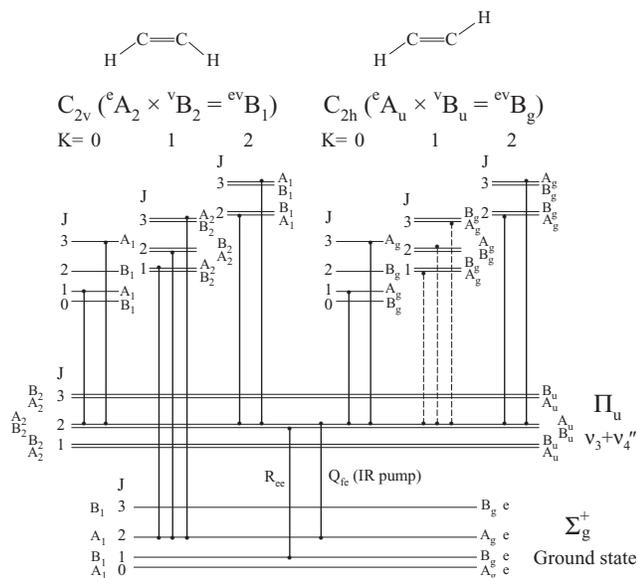


FIG. 3. Energy level diagram showing the rotational structure expected for the $46\,175\text{ cm}^{-1}$ state in one-photon excitation and in IR-UV double resonance via the Q branch of the $\nu_3 + \nu_4''$ level. Left side: assuming it belongs to the S_1 -cis well. Right side: assuming it belongs to the S_1 -trans well. The ground state and the $\nu_3 + \nu_4''$ level (lower part of the figure) are common to the two parts of the diagram. The symmetry species given for them are reductions of the linear molecule species onto the point groups C_{2v} and C_{2h} .

that arise in these two cases in fluorescence excitation spectra from the zero-point level of the ground state and in double resonance spectra via the Q branch of $\nu_3 + \nu_4''$ (Π_u). The figure shows that a B_u upper vibrational state in C_{2h} symmetry will give only $K = 0-1$ and $2-1$ sub-bands in double resonance from $\nu_3 + \nu_4''$, according to the C-type selection rule, $K' - l'' = \pm 1$, though a weaker axis-switching or Coriolis-induced $K = 1-1$ sub-band may be observable given the right circumstances (dashed lines in the figure). However, there will be no transitions from the ground vibrational state of the molecule. In contrast, a B_2 upper vibrational state in C_{2v} symmetry will give $K = 0-1$ and $2-1$ sub-bands in double resonance and a $K = 1-0$ sub-band in one-photon excitation.

The important result is that, for cis-well upper states, bands involving even- K' and odd- K' levels cannot appear in the same spectrum. For trans-well upper states all K' levels (subject to the line strengths given by the direction cosine matrix elements) will appear either in the one-photon spectrum or in the double resonance spectrum, but not both.

C. Tunneling effects and K-staggering

Rigid-molecule arguments, as just described, will be valid up to about the energy of the cis-trans isomerization barrier. Even below that energy, effects arising from tunneling through the barrier will start to become noticeable. Exactly how the levels behave will depend on the mechanism of the cis-trans isomerization. It is not the purpose of this paper to go into the details of the permutation-inversion group theory that is required to describe the observed tunneling effects,³⁸

but essentially there are three possible mechanisms, requiring description by three different permutation-inversion groups. The energy level patterns are predicted to be different in these three cases.

The mechanism that has received most attention^{39,40} treats the torsion as the only large amplitude coordinate, which leads to isomerization by internal rotation, as in H_2O_2 . For C_2H_2 the *ab initio* results predict¹⁴ that the molecule is half-linear at the isomerization barrier, which implies a second mechanism where the large amplitude motions leading to isomerization are local CCH bends, one at each end of the molecule, with the molecule always remaining planar. Naturally, the barrier to internal rotation goes to zero when the molecule is half linear. This leads to a third mechanism in which the internal rotation is added to the two local bends to give a complete description of the isomerization; embodying three large amplitude coordinates, the permutation-inversion group required³⁸ is of order 32.

Assuming the C_2H_2 molecule remains planar, with the isomerization occurring exclusively through the local bends, the predicted level pattern is that even- K levels go with one of the two tunneling components of a vibrational state and odd- K levels go with the other.³⁸ No actual splittings will be observed, but instead there will be a staggering of odd- K levels versus even- K levels. At energies close to the barrier, where internal rotation must also be considered, there will be three tunneling components for each vibrational state, resulting in a further staggering of the $K = 2, 6, 10, \dots$ levels versus the $K = 0, 4, 8, \dots$ levels. (There is no further staggering of the odd- K levels.) The level shifts associated with this additional staggering mechanism will probably not be significant until quite close to the isomerization barrier.

The K structure pattern of the levels in Fig. 1 appears to be an example in which staggering is observed. The S_1 -trans isomer has very large Coriolis interaction between its ν_4 and ν_6 vibrations because of the near-degeneracy of their frequencies. On the other hand, *ab initio* calculation of the S_1 -cis well frequencies (summarized in Table III) indicates a different situation, where the corresponding two frequencies are nearly 250 cm^{-1} apart;³⁶ therefore, there will be only minimal Coriolis interaction in the S_1 -cis isomer. Consequently, we can expect the S_1 -cis vibrational states to behave as unperturbed asymmetric tops, so that the rotational constant $A - 1/2(B + C)$ derived from the $K' = 0$ and 2 levels in Fig. 1 truly reflects the molecular geometry. Taking $r(CC) = 1.3423\text{ \AA}$, $r(CH) = 1.0983\text{ \AA}$, and $\theta(CCH) = 132.62^\circ$, from Ref. 36, we calculate $A - 1/2(B + C)$ for the cis isomer to be 12.79 cm^{-1} . This is very close to the observed value, 12.94 cm^{-1} , derived from Fig. 1, which suggests that the internal rotation tunneling mechanism is not important for this vibrational state. As the arrow in Fig. 1 indicates, the $K' = 1$ level lies 3.9 cm^{-1} above where the asymmetric top energy formula predicts. Since the centrifugal distortion constant Δ_K calculated from the *ab initio* potential is only 0.00826 cm^{-1} , and there is no reason to suspect that the $46\,175\text{ cm}^{-1}$ level is significantly perturbed, our interpretation is that this 3.9 cm^{-1} shift represents the staggering of the K structure that results from tunneling through the isomerization barrier.

TABLE III. *Ab initio*-calculated harmonic vibrational frequencies of the S₁-cis state of C₂H₂.

		Harmonic vibrational frequencies			Calculated isotope shift (Ref. 36)
		Stanton <i>et al.</i> (Ref. 14)	Ventura <i>et al.</i> (Ref. 19)	Ref. 36	¹² C ₂ H ₂ -H ¹² C ¹³ CH
ν_1	CH symmetric stretch (a_1)	3049	3094	2997	5.5
ν_2	CC stretch (a_1)	1659	1577	1583	29.1
ν_3	Symmetric bend (a_1)	816	812	806	0.6
ν_4	Torsion (a_2)	704	860	817	4.3
ν_5	CH antisymmetric stretch (b_2)	2996	3044	2942	4.5
ν_6	Antisymmetric bend (b_2)	441	677	572	3.7

^aExperimentally the ν_6 frequency is estimated, from the energy difference between the 3^16^1 and 3^1 levels (i.e., not corrected for anharmonicity), to be 565 cm^{-1} .

D. Lifetime and quantum beat measurements

In contrast to the nearby levels of the S₁-trans well, which have upper state lifetimes of about 300 ns, the $K' = 1$ upper level of the $46\,192\text{ cm}^{-1}$ band has a radiative lifetime of at least $2\ \mu\text{s}$ (for $J' = 1e$). (This is approximately the longest lifetime that we can measure with our collection optics before the molecules leave the detection region.) The lifetimes of the $K' = 0$ and 2 levels of the double resonance spectrum shown in Fig. 1 have not been measured directly but, from spectra recorded with the detection gated at different delay times, are found to be much longer than those of the surrounding vibrational levels. This result strongly suggests that all three unassigned upper levels belong to the same vibrational level and also provides clear evidence that the upper level is metastable, as expected for a level of the S₁-cis well, where the electronic transition to the ground state is forbidden, being $^1A_2 - ^1A_1$ in C_{2v} symmetry.

Nevertheless, many of the rotational levels of the S₁-trans isomer are perturbed by triplet states, and have lifetimes longer than $1\ \mu\text{s}$.^{41,42} It must then be asked if the $46\,192\text{ cm}^{-1}$ level could be a triplet level. At this energy only the T₃ state has vibrational structure that is sparse enough for spin-orbit interaction to induce a transition to one complete isolated triplet vibrational level. Even so, the rotational structure might be expected to show triplet splittings and possibly local perturbations in such a case. The deciding factor is the rotational magnetic moment, which should be large for a triplet state.⁴¹ We have recorded Zeeman quantum beats from a number of vibrational bands in this region and find that the pattern given by the $46\,192\text{ cm}^{-1}$ level is similar to those given by most of the securely assigned S₁-trans levels in the region. The observed $|g|$ -factor for the R(0) line is only 0.089, which means that the upper state has principally singlet character.

Interestingly, spectra of the $K = 1$ level at $46\,192\text{ cm}^{-1}$ and the S₁-trans 3^16^4 , $K' = 1$ level at $46\,087\text{ cm}^{-1}$ have been recorded using the technique of surface electron ejection by laser-excited metastables (SEELEM).⁴³ (Note: these levels are not correctly assigned vibrationally in Ref. 43, as that paper was published before detailed calculations of the polyad structure³² had established the vibrational assignments.) SEELEM spectra are observed when a metastable species is excited by laser excitation and travels for a time that is huge compared to a typical radiative lifetime, before striking a metal surface and causing the emission of an elec-

tron. The vertical excitation energy of the metastable must be larger than the work function of the metal. In the experiments of Ref. 43, the travel time was $\sim 300\ \mu\text{s}$, and the metal used was gold, which has a work function of $41\,000\text{ cm}^{-1}$. *Ab initio* calculations¹⁹ predict that the only metastable triplet state of C₂H₂ lying high enough in energy to give SEELEM intensity is the T₃ state. The metastable T₁ and T₂ states lie too low to give SEELEM intensity though, since their levels form a near-continuum at $46\,000\text{ cm}^{-1}$, they presumably contribute to the observed magnetic moments of the $46\,192$ and $46\,087\text{ cm}^{-1}$ levels (the $46\,087\text{ cm}^{-1}$ level has $|g| \sim 0.01$). The $46\,192\text{ cm}^{-1}$ band gives a strong, clean SEELEM spectrum, where the rotational intensity pattern closely follows that of the laser excitation spectrum.⁴³ In contrast the much stronger $46\,087\text{ cm}^{-1}$ band gives only a weak disorganized SEELEM spectrum. At present it is not clear why the SEELEM intensities of the two bands are so different; if it should prove that C₂H₂ in its S₁-cis state lives long enough to contribute directly to the SEELEM intensity, SEELEM spectroscopy could possibly provide a method to identify other S₁-cis levels in the laser excitation spectrum.

V. VIBRATIONAL ASSIGNMENTS OF THE CIS WELL STATES

As discussed at the end of Sec. I, the $46\,175\text{ cm}^{-1}$ vibrational level is the best-characterized of the observed states that do not fit into the vibrational manifold of the S₁-trans well. Assuming that this state belongs to the S₁-cis well, it must have B₂ vibrational symmetry, while its small ¹³C isotope shifts imply that it lies quite low in the potential well, probably below 2000 cm^{-1} .

The other three vibrational levels that we have found, which do not fit into the manifold of the S₁-trans well, all lie below the $46\,175\text{ cm}^{-1}$ level. They give rise to very weak bands where we do not observe the complete set of $K' = 0-2$ rotational levels. The most interesting of these levels appears as a $K' = 0$ sub-band at $45\,734.7\text{ cm}^{-1}$ and a $K' = 2$ sub-band at $45\,790.8\text{ cm}^{-1}$, in double resonance via the ground state $\nu_3 + \nu_4''$ level. The assigned lines are listed in Table IV. The $K' = 0$ sub-band is a single Q branch in double resonance via the Q branch of $\nu_3 + \nu_4''$, but appears as R and P branches in double resonance via the R branch of $\nu_3 + \nu_4''$. This is consistent with A₂ upper state vibrational symmetry. The derived value

TABLE IV. (a) Assigned lines of the 45 734.7 cm^{-1} band (cis-4^1), observed in IR-UV double resonance via the Q branch of the $\nu_3 + \nu_4''$ band. Values are in cm^{-1} .

J	K = 0-1	K = 2-1	
	Q	R	Q
1	45 734.57	45 795.09	
2	45 734.26	45 797.02	45 790.38
3	45 733.79	45 798.73	45 789.96
4	45 733.17		45 789.38
5	45 732.46		45 788.63
6	45 731.51		
7	45 730.36		
8	45 729.08		

(b) Assigned $K' = 1$ upper state energy levels of the 45 610 cm^{-1} state (cis-3^1), observed in IR-UV double resonance via R and P lines of the ν_3'' fundamental. Values are in cm^{-1} .

J	$K' = 1e$	$K' = 1f$
1	45 625.09	45 624.98
2	45 629.46	45 629.23
3	45 636.07	45 635.61
4	45 644.88	45 644.14
5	45 655.83	

(c) Assigned lines of the trans-1^13^1 , $K = 0-\nu_4''$ and cis-6^2 , $K = 0-\nu_4''$ bands. Values are in cm^{-1} .

J	R		Q		P	
1	45 506.31	45 507.03	45 502.00	45 502.75	45 499.84*	45 500.59
2	45 508.09	45 508.77	45 501.66*	45 502.36	45 497.24	45 498.00
3	45 509.66	45 510.32	45 501.08*	45 501.78	45 494.49	45 495.22
4	45 511.01	45 511.64	45 500.34	45 500.97*	45 491.57	45 492.25
5	45 512.16	45 512.99*	45 499.37	45 499.99		45 488.99
6	45 512.99*	45 513.74*	45 498.16*	45 498.81	45 484.94	45 485.66
7			45 496.81	45 497.42	45 481.47	
8			45 495.22*		45 477.51	45 478.32
9			45 493.26			

The $\text{trans-1}^13^1-\nu_4''$ band is the higher frequency component at low J values. An avoided crossing with cis-6^2 occurs between $J' = 5$ and 6. Blended lines are marked with an asterisk. The Q(9) line was not included in the least squares fit given in Table V.

of $A - 1/2(B + C)$ is 14.03 cm^{-1} , from which we can predict the expected position of the corresponding $K' = 1$ sub-band, but nothing is found at this energy in either one-photon fluorescence excitation or double resonance spectra. The $K' = 0$ levels have an exceptionally long fluorescence lifetime, compared to other nearby trans states. This further suggests that they cannot belong to states localized in the S_1 -trans well.

The other unassigned vibrational levels appear just as single sub-bands. One of these is a $K' = 1$ sub-band at $45 622.7 \text{ cm}^{-1}$, which is found in double resonance via the ν_3'' fundamental. The upper state vibrational symmetry is therefore either A_1 or B_1 . However, the upper levels of the Q lines lie below the upper levels of the R and P lines, which requires that the vibrational symmetry is A_1 , assuming that the asymmetry splitting behaves normally. This assumption appears to be valid, because the asymmetry coefficient, $B - C = 0.073 \text{ cm}^{-1}$, is only slightly smaller than what would be expected for an unperturbed vibrational level of the S_1 -cis well (0.085 cm^{-1}). The intensity of this sub-band appears to come from interaction with the topmost $K = 1$ level of trans-3^1B^3 , which lies only 8.1 cm^{-1} below.³² We have not found the corresponding $K' = 0$ and 2 sub-bands; the $K' = 0$ sub-band should lie near $45 610 \text{ cm}^{-1}$.

The other unassigned vibrational level which appears as a single sub-band is a $K' = 0$ level at $46 114.0 \text{ cm}^{-1}$ that perturbs the $K' = 0$ level of the trans-1^13^1 vibrational state between $J' = 5$ and 6. It is found as a hot band from the ν_4'' fundamental in the one-photon excitation spectra. The perturbation in trans-1^13^1 had been noted in Ref. 29, but no extra lines were observed, and little could be said because of blending in their higher temperature spectra. Our jet-cooled spectra give the branch structures of both states up to $J' = 7$ and show that the perturbing state has A_1 vibrational symmetry. The interaction matrix element between the two states is 0.30 cm^{-1} . We have looked without success for the $K' = 2$ levels of the unassigned state near the corresponding levels of trans-1^13^1 .

The fact that we do not find the complete $K' = 0-2$ level structure for these three bands is disappointing but perhaps not unexpected. The sub-bands that can be observed are quite weak, and there is no reason why all three sub-bands with $K' = 0-2$ should have comparable intensities, since levels with even and odd K' values obtain their intensity by interaction with different trans-well vibrational levels. In passing we note that the absence of the complete $K' = 0-2$ level structure for these bands argues against the possibility that the intensity

TABLE V. (a) Rotational constants from least squares fitting of the S₁-cis bands at 46 175, 45 735, and 45 623 cm⁻¹.

State	46 175 cm ⁻¹ (cis-3 ¹ 6 ¹)		45 735 cm ⁻¹ (cis-4 ¹)		45 610 cm ⁻¹ (cis-3 ¹)	
	¹² C ₂ H ₂	H ¹² C ¹³ CH	¹³ C ₂ H ₂	¹² C ₂ H ₂	¹² C ₂ H ₂	¹² C ₂ H ₂
T ₀ (K = 0)	46 175.362	± 0.023	± 0.026	45 734.701	± 0.042	45 622.670
T ₀ (K = 1)	(46 192.206)		Fixed	15.135	0.011	13.95
A	14.019	0.010	Fixed	1.185	0.002	Fixed
B	1.1258	0.0011	0.0033	1.02	Fixed	0.003
C	1.0370	0.0013	0.0004	1.02	Fixed	0.005
Δ _{JK}	0.00074	0.00030				
T _{odd-even}	3.906	0.020				
r.m.s.	0.0191	0.0147	0.0174	0.0253		0.0213

Values are in cm⁻¹. Error limits are three standard deviations. Constants not listed were not included in the fits.

The parameter T_{odd-even} gives the K-staggering, defined as the distance that the K' = 1 level lies above its expected position according to the asymmetric top energy expression. The even and odd K levels were fitted to the same set of rotational constants, except that T_{odd-even} was added to the energy of the K' = 1 levels. The parameter T₀(K = 1) is equivalent to T₀(K = 0) + A - $\frac{1}{2}$ (B + C) + T_{odd-even}. The band at 45 623 cm⁻¹ is the K = 1-0 sub-band of the cis-3₁¹ band, of which the origin is estimated to lie at 45 610 cm⁻¹.

(b) Rotational constants from deperturbation of the interacting trans-1¹3¹, K = 0 and cis-6², K = 0 levels, neglecting asymmetry effects.

T ₀ (cis-6 ² , K = 0)	46 114.01	± 0.05
I/2(B + C) (cis-6 ² , K = 0)	1.0853	0.0018
T ₀ (trans-1 ¹ 3 ¹ , K = 0)	46 114.51	0.05
I/2(B + C) (trans-1 ¹ 3 ¹ , K = 0)	1.0716	0.0014
W ₁₂	0.296	0.019
r.m.s.	0.0151	

Values are in cm⁻¹. The interaction matrix element, W₁₂, is assumed to have no J-dependence. The fit was carried out on term values calculated from Table IV(c) together with energy levels for ν₄' from Ref. 24. Error limits are three standard deviations.

comes from vibronic coupling with higher lying electronic states. If the intensity comes through vibronic coupling, we would not expect to see a K-dependence of the observed intensities.

To obtain the vibrational assignments of these states we must be guided partially by the *ab initio* calculations^{14,19,36} of the cis-well vibrational frequencies and their isotope shifts, which are summarized in Table III. Table III shows that we do not need to consider the two CH stretching vibrations, ν_1 and ν_5 , because they will lie near 2900 cm^{-1} , while the CC stretching vibration, ν_2 , will have much too large an isotope shift for the $46\,175\text{ cm}^{-1}$ state. The key lies in the $45\,735\text{ cm}^{-1}$ state which has A_2 vibrational symmetry. The only vibrational states with A_2 symmetry expected below 2000 cm^{-1} are the torsional fundamental, 4^1 , and the combination levels 3^14^1 and 4^16^2 . If the $45\,735\text{ cm}^{-1}$ state is 4^1 , which is calculated to have a vibrational energy of close to 800 cm^{-1} , the zero-point level of the S_1 -cis well will lie near $44\,900\text{ cm}^{-1}$. If the $45\,735\text{ cm}^{-1}$ state is one of the combination levels, the S_1 -cis zero-point level will lie at least 800 cm^{-1} lower. The most recent *ab initio* calculations of Ref. 36 give the energy of the S_1 -cis zero-point level as $44\,856 \pm 50\text{ cm}^{-1}$. Since the probable uncertainty in this value is far smaller than 800 cm^{-1} , the only reasonable assignment is that the $45\,735\text{ cm}^{-1}$ level is the torsional fundamental, 4^1 . Given this assignment, it is clear that there is excellent agreement between the calculations and the observed spectrum; both predict the S_1 -cis zero-point level to lie near $44\,900\text{ cm}^{-1}$.

Returning to the $46\,175\text{ cm}^{-1}$ level, which has B_2 vibrational symmetry, this level is now known to have about 1300 cm^{-1} of vibrational energy. The only possible B_2 states below about 2000 cm^{-1} are 6^1 , 3^16^1 , and 6^3 . Of these an assignment as 3^16^1 gives good agreement with the calculated frequencies.

The lower of the two A_1 levels, at $45\,610\text{ cm}^{-1}$, must then be the ν_3 fundamental. Its energy allows the cis- ν_6 frequency to be estimated roughly as $46\,175 - 45\,610 = 565\text{ cm}^{-1}$. Although this value agrees remarkably well with the harmonic frequency calculation of Ref. 36, this agreement must be to a large extent fortuitous, because the levels 3^1 and 3^16^1 lie on the cis-well pathway to the isomerization barrier, and must suffer very considerably from anharmonicity, in similar fashion to the corresponding trans-well levels.³² We note that the anharmonicity constant x_{36} for the S_1 -cis state is calculated *ab initio*⁴⁴ to have the exceptionally large value of -54.2 cm^{-1} .

The upper of the two A_1 levels, at $46\,114.0\text{ cm}^{-1}$ (a vibrational energy of $\sim 1200\text{ cm}^{-1}$), then fits as the overtone 6^2 . In principle it would be possible to estimate the position of the zero-point level from this assignment, but in the presence of such strong anharmonic effects such an estimate would be of dubious value. Figure 4 shows the observed and predicted vibrational level structure of the S_1 state of acetylene, as presently understood, up to a vibrational energy of about 5000 cm^{-1} (near the energy of the isomerization saddle point). The Franck-Condon allowed trans levels,^{21–26} which are responsible for the strong bands in the absorption spectrum, are shown in the columns based on ν_2 and ν_3 . Some further trans levels based on ν_1 and ν_5 surround them, while

the trans bending levels and their combinations with ν_2 and ν_3 fill most of the rest of the figure. At the far right are the observed cis-well levels and their assignments. It is interesting that of the six expected lowest-lying vibrational levels of the cis isomer all have been observed except for the zero-point level and the 6^1 level.

As for the isotope shift of the $46\,175\text{ cm}^{-1}$ level (3^16^1), the calculated vibrational contribution to its $^{12}\text{C}_2\text{H}_2\text{-H}^{12}\text{C}^{13}\text{CH}$ shift (from Table III) is 4.3 cm^{-1} . Assuming that the isotope shift of the zero-point level is the same as that of the trans-well, -6.8 cm^{-1} , the calculated $^{12}\text{C}_2\text{H}_2\text{-H}^{13}\text{C}^{12}\text{CH}$ shift is -2.5 cm^{-1} , which is to be compared to the observed -3.03 cm^{-1} .

The rotational constants derived from least squares fits to the lines of the various S_1 -cis well bands are given in Table V.

VI. ON THE ORIGIN OF THE K-STAGGERING

One of the most interesting results of this work is the observation of an even-odd staggering in the K-structure of the cis- 3^16^1 level, which indicates that tunneling through the cis-trans isomerization barrier takes place. Both the Discrete Variable Representation (DVR) calculations of Ref. 36 and the group theory considerations of Ref. 38 predict that such a staggering should occur, but it is not immediately obvious why it arises. A qualitative discussion may help to clarify its origin.

Assume initially that the only vibrational motions possible for C_2H_2 are CCH bending motions at the two ends of the molecule and that it always remains planar. Cis-trans isomerization can take place if one of the CCH bending angles is reversed. Next assume that C_2H_2 is in an electronic state where the equilibrium configuration is cis-bent, and there is no potential minimum at the trans configuration. It is no longer possible to reverse just one of the CCH bending angles, but if both of the CCH bending angles are reversed at the same time, the cis-bent planar C_2H_2 molecule is converted into another, equivalent, cis-bent planar configuration. This new configuration will have exactly the same energy states as the original configuration. If the potential energy barrier between these two cis configurations is small, such that the molecule can tunnel through it, one has the possibility of inversion-like doubling of the vibrational levels of the two configurations, just as in the familiar case of NH_3 .^{5–9} Unlike NH_3 , though, one can take acetylene back to its original configuration by a C_2 rotation about the inertial a-axis, which means that the new configuration is the same as the original one. Since there is only one possible configuration, the energy states of the second configuration must be “thrown away.”

Detailed examination of their effects on the various molecule-fixed coordinates³⁸ shows that the reversal of the CCH bending angles and the C_2 rotation about the a-axis are inextricably linked. To be exact, when these two operations are carried out in sequence, it looks as though nothing has happened to the molecule, or in other words, that the identity operation has been carried out. However, point group arguments do not apply if tunneling occurs. In the language of extended permutation-inversion groups this iden-

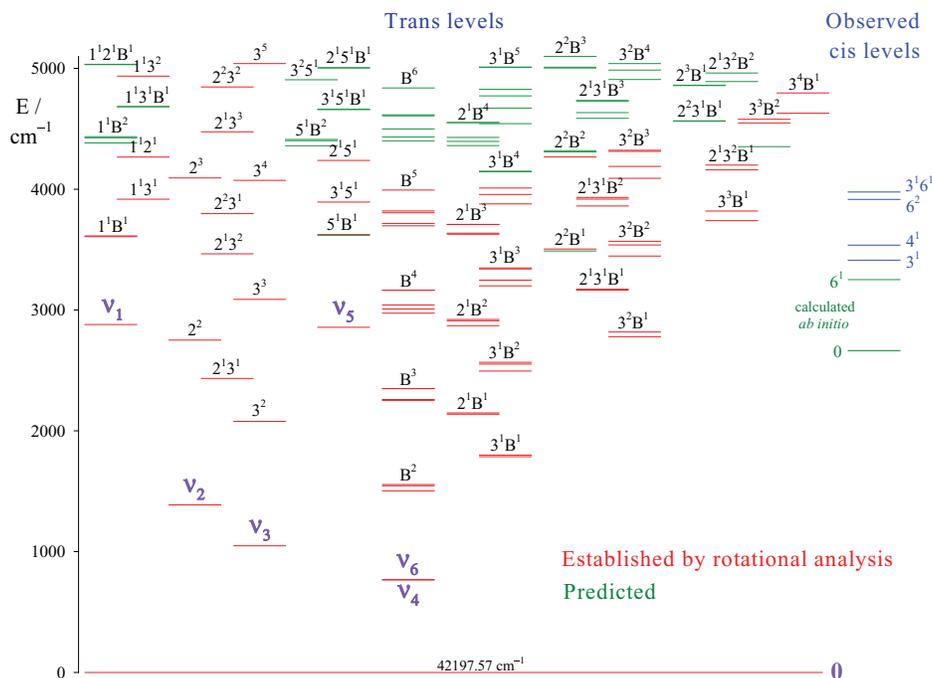


FIG. 4. Observed and predicted $K = 0$ levels of the S_1 state of C_2H_2 up to a vibrational energy of 5000 cm^{-1} . Red lines indicate vibrational levels of the trans isomer which have been established by rotational analysis; the four observed cis well vibrational levels (at the right hand side of the figure) are indicated by blue lines. Green lines indicate the positions predicted for as-yet-unassigned or unobserved states. The diagram is complete for the trans isomer to 5000 cm^{-1} ; a few predicted states above that energy are shown if they belong to polyads that extend below 5000 cm^{-1} .

tity is a “limited” identity (i.e., limited to the non-tunneling situation), because the coordinates corresponding to the two operations, individually, have not returned to their original values.⁴⁶ This complicates the “throwing away” process. The limited identity is one of the symmetry operations of the extended permutation-inversion group. Symmetry arguments³⁸ show that even- K_a and odd- K_a rotational functions are, respectively, symmetric and antisymmetric under this limited identity operation; the same applies to the sum and difference inversion-like tunneling functions. Also, acceptable rotation-tunneling product functions must be symmetric under this limited identity operation. The result is that the acceptable states (which are not thrown away) are those with even- K_a belonging to the symmetric (sum) tunneling component, and those with odd- K_a belonging to the antisymmetric (difference) tunneling component. In essence, the K -staggering in the cis- $3^1 6^1$ vibrational level is what remains of the energy level pattern of the cis-to-cis inversion-like tunneling doubling after half the K -structure in each component has been thrown away. There is no K -staggering in vibrational levels of NH_3 , where all K values are present in both inversion components.

The S_1 state of acetylene has cis and trans isomers occurring on the same electronic potential surface but with a large potential maximum at the linear configuration. In this case the possibility of reversing both CCH bending angles in the two isomers leads to four potential minima, two cis and two trans. These are illustrated in Fig. 3(a) of Ref. 19, Fig. 1 of Ref. 36 and Fig. 4 of Ref. 38. When the molecule in one of the cis wells tunnels through the interconversion barrier to the other cis well, it passes across one of the trans wells but since

the energy level structure of the cis wells is quite different from that of the trans wells, there is no inversion-like doubling between the cis and trans isomers as a result of tunneling through the barrier because the cis and trans isomers are not equivalent. The cis-to-cis inversion-like doubling, giving rise to K -staggering, must still occur but there will be no splittings. There will be a corresponding trans-to-trans inversion-like doubling with similar K -staggering in the trans-well levels. More detail is given in Ref. 38, which includes a discussion of the additional staggering that occurs when tunneling through the isomerization barrier as a result of internal rotation must also be considered.

It may be argued that the K -staggering in C_2H_2 should not be compared with the inversion of NH_3 but rather with the level pattern of a triatomic molecule such as H_2O when it has sufficient bending excitation to become linear. In the H_2O case the K -structure changes smoothly at the barrier to linearity from an asymmetric top pattern to a linear molecule pattern, and there are no discontinuities that alternate with K . However, this is not what happens in C_2H_2 , where the level pattern is like that of NH_3 , but with the even- K levels missing in one inversion component of a vibrational level and odd- K levels missing in the other.

VII. DISCUSSION

This work illustrates for the first time some of the high resolution spectroscopic signatures of cis-trans isomerization. The state involved, the S_1 state of acetylene, is well suited for a study of this type because its vibrational structure is comparatively sparse near the cis-trans saddle point, and

the bands can be observed in transitions from a different electronic state where no cis-trans isomerism is possible, thereby simplifying the analysis.

To summarize, transitions from the ground electronic state of acetylene are allowed to the lower energy (trans) isomer of the S_1 state, but not to the cis isomer, which lies about 2700 cm^{-1} higher. The interconversion barrier (saddle point) lies about 2000 cm^{-1} still higher in energy, with the transition state being half-linear.¹⁴ The “isomerization coordinate” which carries the shape of the molecule from that of the trans isomer to that of the transition state is a linear combination of two normal coordinates, Q_3 (trans bend) and Q_6 (cis bend). Very large higher-order cross-terms between Q_3 and Q_6 are therefore needed in the potential function in order to represent the minimum energy pathway along the isomerization coordinate. As a result, the vibrational levels that involve excitation of both ν_3 and ν_6 are highly anharmonic.^{32,35} Very detailed analyses of the level structure of the trans-well are required in order to identify each level³² and, so far, every expected level of the trans-well has been accounted for up to a vibrational energy of 4200 cm^{-1} . A few weak “extra” bands at lower energy are left over. The upper states of these extra bands do not belong to a triplet electronic state, because they are observed to have only small Zeeman effects; their carbon isotope shifts are not compatible with their energy relative to the zero-point level of the trans isomer; *ab initio* calculations predict no other singlet electronic states in this energy region,¹⁹ and the upper states have extremely long lifetimes, indicating that they are metastable. The conclusion is that these extra vibrational levels belong to the S_1 -cis isomer and comparison with the results of *ab initio* calculations^{36,45} strongly supports this conclusion.

The upper state of the most obvious cis-well band assigned so far is cis- 3^16^1 ($46\,175\text{ cm}^{-1}$). This is not altogether surprising because the isomerization pathway in the cis isomer is also a combination of Q_3 and Q_6 , where these coordinates are the symmetric and antisymmetric in-plane bends. The cis- 3^16^1 state lies only about 700 cm^{-1} below the interconversion barrier and has a high probability of tunneling through it. The tunneling has two consequences. One is that the cis- 3^16^1 state can interact with levels of the trans-well close by in energy and thereby obtain appreciable absorption intensity. As discussed in Sec. IV C, the other is that its K structure shows a staggering of the odd-K levels versus the even-K levels,³⁸ amounting to no less than 3.9 cm^{-1} .

As yet no K-staggerings have been identified in trans-well levels. The reason for this is that the bending states of the trans isomer suffer from strong Coriolis and Darling-Dennison resonance, so that it is difficult to establish the zero-order positions of the K-rotational levels. Nevertheless, the progressive breakdown of the simple Coriolis plus Darling-Dennison model for the higher bending combination polyads of the trans isomer³² must reflect the onset of K-staggerings. Not every predicted level near the energy of the interconversion barrier will show K-staggerings, of course; the magnitudes of these staggerings will depend on the specific vibrational quantum numbers and on how effectively the molecule in a particular state can tunnel through the barrier.

In addition to this even-odd K-staggering arising from local-bend tunneling, there will be a further staggering of the $K = 2, 6, 10, \dots$ levels versus the $K = 0, 4, 8, \dots$ levels, when tunneling due to internal rotation becomes important near the cis-trans saddle point.³⁸ Table V shows that the A rotational constant of the torsional fundamental, cis- 4^1 , is about 1 cm^{-1} larger than that of cis- 3^16^1 , which (as described in Sec. IV C) is close to the value calculated from the *ab initio* geometric structure. The $K' = 2$ level of cis- 4^1 ($45\,790.8\text{ cm}^{-1}$) lies not far above the upper $K' = 2$ level of trans- 2^2B^1 ($45\,777.9\text{ cm}^{-1}$);³² thus, we cannot rule out the possibility that it has been pushed up by interaction with it. Nevertheless, the effects of internal rotation are expected to be magnified on excitation of the torsional vibration and, when only the $K' = 0$ and 2 levels are observed, any staggering due to internal rotation tunneling will appear as a change in the apparent A rotational constant derived from their separation.³⁸ Therefore, it is not impossible that there is a K-staggering of about 4 cm^{-1} due to internal rotation tunneling in the cis- 4^1 vibrational level. Nothing can be said in this instance about possible staggering due to the local-bend tunneling (odd-K versus even-K) since the $K' = 1$ level of cis- 4^1 has not been located.

A number which could be of some significance is the interaction matrix element between the cis- 6^2 and trans- 1^13^1 levels, which is found, from the minimum rotational level separation at the perturbation between them, to be 0.30 cm^{-1} . (See Table V.) In a simple model this matrix element would be the product of an electronic factor, a cis-to-cis tunneling matrix element and a cis-trans vibrational overlap integral, divided by a cis-trans energy denominator. It will be instructive to attempt to reproduce this number by *ab initio* calculation.

The vibrational energy level pattern expected at higher energies can be predicted roughly from the DVR calculations reported in Ref. 36. Those states which have many quanta of ν_3 and ν_6 will show progressively larger K-staggerings, which will rapidly become so large that it will be difficult to associate a given set of even-K levels with a corresponding set of odd-K levels. Their vibrational wave functions, instead of being mostly localized either in the two cis-wells or in the two trans-wells, will have amplitude in all four wells, and the mixed state vibrational characters of the even- and odd-K levels will become increasingly different. The assignment of approximate vibration-rotation quantum numbers will require very detailed calculations. Since the barrier to internal rotation vanishes at the half-linear transition state, there will be a further staggering of the $K = 2, 6, 10, \dots$ levels versus the $K = 0, 4, 8, \dots$ levels, as just described. In contrast, the progressions that do not involve the bending vibrations will continue normally, as at lower energy, barring minor perturbations and resonances.

The level pattern above the interconversion barrier will presumably reorganize itself according to a new basis set, just as the levels of the ν_2 (“umbrella”) vibration of ammonia above the inversion barrier can be treated as those of a planar molecule vibrating with large amplitude. It would seem that the bending levels of acetylene above the cis-trans isomerization barrier should rearrange themselves into those of a non-linear molecule vibrating with three very large amplitude coordinates. The vibrational wave functions will sample all of

the available bending phase space, so that any given level can no longer be labeled specifically as cis or trans. Above the potential maximum at the linear configuration the level pattern will become that of a linear molecule but, at that high energy, interactions with other electronic states will almost certainly obscure the pattern.

In conclusion, the spectrum of a molecule capable of cis-trans isomerization consists of superimposed spectra from the two isomers in the energy region below the interconversion barrier. Those vibrations corresponding to the minimum energy pathway to isomerization are extremely anharmonic, and those levels near the barrier which can tunnel through it display staggerings in their K-rotational structure. At the interconversion barrier the levels merge into a very different-looking large amplitude vibrational pattern. Those vibrations that are not involved in the isomerization path behave normally, so that the spectrum consists of overlapping progressions with different degrees of complexity.

Many aspects of the spectrum are different from those of molecules showing inversion doubling or internal rotation. We are continuing work on the interesting region of the S₁ state of acetylene where the vibrational level pattern is reorganizing itself near the barrier to isomerization.

ACKNOWLEDGMENTS

We thank Dr. Jon Hougen (NIST, Gaithersburg) for valuable discussions on the group theory aspects, and Dr. Michelle (Silva) Clark for recording the ¹³C₂H₂ data. At MIT, this work was supported by the U.S. Department of Energy (DOE) Grant No. DE-FG0287ER13671. A.J.M. thanks the Academia Sinica, Taiwan, for the award of a Distinguished Visiting Professorship, and the Natural Sciences and Engineering Research Council of Canada for partial support of this work. J. H. Baraban acknowledges the support of a NSF Graduate Research Fellowship.

¹J. H. van 't Hoff, Arch. Néerl. Scie. Exactes Nat. Ser. 3A **9**, 445 (1874).

²J. Wislicenus, Ber. **20**, 1008 (1887); J. Wislicenus, Abhandl. königl. sachs. Gesell. Wissensch. Leipzig, Math-Phys Classe **14**, 1 (1887).

³For a historical account see A. J. Ihde, J. Chem. Educ. **36**, 330 (1959).

⁴W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1970).

⁵C. E. Cleeton and N. H. Williams, Phys. Rev. **45**, 234 (1934).

⁶B. Bleaney and R. P. Penrose, Nature (London) **157**, 339 (1946).

⁷W. E. Good, Phys. Rev. **70**, 213 (1946).

⁸C. C. Costain, Phys. Rev. **82**, 108 (1951).

⁹E. Schnabel, T. Törring, and W. Wilke, Z. Phys. **188**, 167 (1965).

¹⁰D. Demoulin and M. Jungen, Theor. Chim. Acta **34**, 1 (1974).

¹¹H. Lischka and A. Karpfen, Chem. Phys. **102**, 77 (1986).

¹²Y. Yamaguchi, G. Vacek, and H. F. Schaefer, Theor. Chim. Acta **86**, 97 (1993).

¹³G. Vacek, J. R. Thomas, B. J. DeLeeuw, and Y. Yamaguchi, J. Chem. Phys. **98**, 4766 (1993).

¹⁴J. F. Stanton, C. Huang, and P. G. Szalay, J. Chem. Phys. **101**, 356 (1994).

¹⁵C. D. Sherrill, G. Vacek, Y. Yamaguchi, H. F. Schaefer III, J. F. Stanton, and J. Gauss, J. Chem. Phys. **104**, 8507 (1996).

¹⁶Q. Cui, K. Morokuma, and J. F. Stanton, Chem. Phys. Lett. **263**, 46 (1996).

¹⁷Q. Cui and K. Morokuma, Chem. Phys. Lett. **272**, 319 (1997).

¹⁸K. Malsch, R. Regentisch, P. Swiderek, and G. Hohlneicher, Theor. Chem. Acc. **100**, 171 (1998).

¹⁹E. Ventura, M. Dallos, and H. Lischka, J. Chem. Phys. **118**, 1702 (2003).

²⁰B. Schubert, H. Köppel, and H. Lischka, J. Chem. Phys. **122**, 184312 (2005).

²¹G. W. King and C. K. Ingold, Nature (London) **169**, 1101 (1952).

²²C. K. Ingold and G. W. King, J. Chem. Soc. **1953**, 2702.

²³K. K. Innes, J. Chem. Phys. **22**, 863 (1954).

²⁴J. K. G. Watson, M. Herman, J. C. Van Craen, and R. Colin, J. Mol. Spectrosc. **95**, 101 (1982).

²⁵J. C. Van Craen, M. Herman, R. Colin, and J. K. G. Watson, J. Mol. Spectrosc. **111**, 185 (1985).

²⁶J. C. Van Craen, M. Herman, R. Colin, and J. K. G. Watson, J. Mol. Spectrosc. **119**, 137 (1986).

²⁷A. L. Utz, J. D. Tobiasson, E. Carrasquillo M., L. J. Sanders, and F. F. Crim, J. Chem. Phys. **98**, 2742 (1993).

²⁸J. D. Tobiasson, A. L. Utz, and F. F. Crim, J. Chem. Phys. **99**, 928 (1993).

²⁹A. J. Merer, N. Yamakita, S. Tsuchiya, J. F. Stanton, Z. Duan, and R. W. Field, Mol. Phys. **101**, 663 (2003).

³⁰A. J. Merer, N. Yamakita, S. Tsuchiya, A. H. Steeves, H. A. Bechtel, and R. W. Field, J. Chem. Phys. **129**, 054304 (2008).

³¹A. H. Steeves, A. J. Merer, H. A. Bechtel, A. R. Beck, and R. W. Field, Mol. Phys. **106**, 1867 (2008).

³²A. H. Steeves, H. A. Bechtel, A. J. Merer, N. Yamakita, S. Tsuchiya, and R. W. Field, J. Mol. Spectrosc. **256**, 256 (2009).

³³A. J. Merer, Z. Duan, R. W. Field, and J. K. G. Watson, Can. J. Phys. **87**, 437 (2009).

³⁴J. Cariou and P. Luc, *Atlas du Spectre d'Absorption de la Molécule de Tellure: 21 100–23 800 cm⁻¹* (CNRS, Orsay, 1980).

³⁵M. Mizoguchi, N. Yamakita, S. Tsuchiya, A. Iwasaki, K. Hoshina, and K. Yamanouchi, J. Phys. Chem. A **104**, 10212 (2000).

³⁶J. H. Baraban, A. R. Beck, A. H. Steeves, J. F. Stanton, and R. W. Field, J. Chem. Phys. **134**, 244311 (2011).

³⁷G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand Inc., New York, 1965).

³⁸J. T. Hougen and A. J. Merer, J. Mol. Spectrosc. **267**, 200 (2011).

³⁹K. Yamada, T. Nakagawa, and K. Kuchitsu, J. Mol. Spectrosc. **51**, 399 (1974).

⁴⁰J. K. Lundberg, in *Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping*, edited by H.-L. Dai and R. W. Field (World Scientific, Singapore, 1995), Chap. 22.

⁴¹N. Ochi and S. Tsuchiya, Chem. Phys. **152**, 319 (1991).

⁴²M. Drabbels, J. Heinze, and W. L. Meerts, J. Chem. Phys. **100**, 165 (1994).

⁴³W. L. Virgo, K. L. Bittinger, A. H. Steeves, and R. W. Field, J. Phys. Chem. A **111**, 12534 (2007).

⁴⁴J. H. Baraban and J. F. Stanton, private communication (2011).

⁴⁵M. Kállay and J. Gauss, J. Chem. Phys. **121**, 9257 (2004).

⁴⁶J. T. Hougen, J. Mol. Spectrosc. **256**, 170 (2009).