VI. TECHNICAL PROGRESS REPORT

1. Acetylene ↔ Vinylidene Isomerization Detected by Spectral Cross-Correlation

The vinylidene radical ($H_2C=C:$) is the simplest unsaturated hydrocarbon, and as such, has been the focus of much experimental and theoretical work [1-15]. In spite of this, the height of the vinylidene ⇒ acetylene isomerization barrier is still uncertain. Theoretical calculations range from 0 [11] to 8 kcal/mole [9] above the vinylidene minimum. These values imply a very short vinylidene lifetime (0.01-10 psec), so that detection of vinylidene will be difficult. Thus far, only the photodetachment studies of Lineberger et al [14] have yielded any information about vinylidene in the S_0 state. These studies confirmed the transitory nature of singlet vinylidene and also determined the frequencies of the C-C (v_2) stretch and scissors (v_3) vibrations. However, even the most recent photodetachment studies [15] are limited by rotational congestion.

We have developed a new procedure to detect acetylene ↔ isomerization in stimulated emission pumping (SEP) spectra [16,17] which we call spectral cross-correlation (SCC). SEP is used to access two disjoint sets of highly excited acetylene vibrational levels (in the $\tilde{X}\ ^1\Sigma_g^+$ ground electronic state) at an energy near the suspected isomerization threshold energy. By cross-correlating the spectra, information about vibrational mode mixing is extracted. The lowest few vinylidene vibrational levels act as "resonances" which promote mode-mixing among acetylene levels. The energy-localized mode-mixing induced by a vinylidene level provides a way of locating and characterizing these vinylidene levels which would otherwise be invisible in our SEP spectra. This mode mixing can be analyzed using a symmetry based argument to determine the extent of acetylene↔vinylidene mixing. The symmetry behavior of the acetylene ↔ vinylidene interaction distinguishes it from the ubiquitous acetylene ↔ acetylene Fermi and Coriolis interactions.

The physical idea behind SCC is quite simple: two SEP spectra are recorded via intermediate states of the same rigorous symmetry (angular momentum, J, and rovibronic species, Γ_{rve}) , but maximally different approximate symmetries (e.g. bend vs. stretch, different isolated local modes, K_a =0 vs. K_a =1, etc.). These spectra will show similar features with different intensities; however, if the approximate symmetry is conserved,

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all strong transitions in one spectrum will be weak or absent in the other spectrum and *vice-versa*. Thus, the cross-correlation will be near zero. As the internal energy of the region probed is increased, the approximate symmetry will be increasingly broken and independent distributions of intensity in the two spectra will produce a "universal" high energy limit for the cross-correlation. The analysis of SCC as a function of energy therefore will show the evolution of the approximate symmetry from a conserved to a non-conserved quantity. However, this evolution will not necessarily be monotonic, because resonances will occur due to zero order "promoter" levels which are particularly effective in breaking the approximate symmetry. The bound states of vinylidene will play just such a role in the SCC of the SEP spectra of HCCH. By analyzing the vinylidene and acetylene quantum states using the full G_8 symmetry group (the complete nuclear permutation inversion group of $^{12}C_2H_2$ [16a]), and the fact that vinylidene zero-order levels will be sparse in the energy range under study leads to the conclusion that only certain symmetry species of acetylene will be perturbed by each vinylidene vibrational level. Thus isomerization for one symmetry species of acetylene is allowed (hence detectable) while it is forbidden for the other species. (All symmetry species of vinylidene isomerize.)

SEP spectra of acetylene in the energy region between 15000 cm^{-1} and 15900 cm^{-1} of acetylene vibrational excitation were recorded and the spectral cross correlation analyzed. The SCC index shows signs of rotational symmetry alternation which is diagnostic of acetylene↔vinylidene isomerization. Unfortunately, a mutual perturbation between the $\tilde{A}$ state intermediate levels prevented the extraction of a tight upper bound for the vinylidene lifetime with the specific spectral cross-correlation function used. Preliminary studies with other spectral cross-correlation functions suggest that this feature is really the superposition of two resonances (due to K=0 and K=2 vinylidene) separated by ~80 cm^{-1}, each with a width of ~30 cm^{-1}, which corresponds to a lifetime of ~200 fs. Recently, Lineberger [15a] has measured the gas phase acidity of vinyl radical, which allows the completion of a thermochemical cycle (see figure 1 on page). The value obtained by Lineberger for the acetylene to vinylidene isomerization energy (44±4 kcal/mole) is in remarkable agreement with the upper bound value obtained from our cross-correlation measurements (44.4±0.6 kcal/mole).

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By applying these same ideas to the symmetry species of $^{13}C_2H_2$, we have shown that SEP experiments on this isotopomer will provide more detailed information on the acetylene-vinylidene isomerization.

Selective preparation of localized HCC vs CCD bending states of HCCD would be another method for studying the acetylene↔vinylidene isomerization and the associated large amplitude motions. Localized bending of a single hydrogen is forbidden by symmetry in HCCH and DCCD, but a cursory examination of the known details of the$\tilde{A}$ state potential surface[18] suggests that it might be possible to pump transitions which would have Franck-Condon overlap only with a single local bending progression of HCCD. To determine if this is possible, a better characterization of the A state of acetylene is necessary, and we have measured and completed a full vibrational analysis of the $\tilde{A}$-$\tilde{X}$ transition of the HCCD isotopomer.

Fluorescence excitation spectroscopy of a rotationally cooled isotopic mixture of HCCH, HCCD, and DCCD, combined with convential high resolution absorption spectra, led to a determination of all six normal mode vibrational frequencies for the acetylene $\tilde{A}$ state [20]. The rotational subband ($K^1{}_0$ vs. $K^0{}_1$) could be identified without ambiguity due to the absence of the R(0) or P(1) line and a complete set of A state vibrational constants was obtained. Analysis of progressions in the $\tilde{A}$ and $\tilde{X}$ state vibrations has yielded the HCCD $\tilde{A}$ state vibrational frequencies ν_1, ν_2, ν_3, ν_5, and ν_6. Teller-Redlich product rules[19] relate the various isotopomer rotational constants and vibrational frequencies, allowing determination of the unknown frequencies ν_5(HCCH), ν_4 and ν_6(DCCD), and ν_4(HCCD), thus providing a complete set of vibrational frequencies for all three isotopomers.

2.DISSOCIATION OF ACETYLENE

The C-H bond energy ($D^0{}_0$ (H-CCH)) in acetylene is an important, and still uncertain thermochemical quantity. We introduced a novel method for measuring this energy [21], Zeeman anti-crossing spectroscopy (ZAC) in which a magnetic field is used to tune a predissociated, optically inaccessible triplet level into resonance with an optically accessible singlet level. This experiment produced an extremely precise (±0.004 kJ/mole) upper bound of 553.5 kJ/mole for the bond energy. This is in good agreement with other determinations [22,23,24] and theoretical work [25]. Figures 6 and 7 illustrate comparisons of recent determinations.

In an attempt to tighten the upper bound obtained by ZAC spectroscopy, we have recently performed Stark anti-crossing spectroscopy (SAC) measurements on acetylene vapor (~20 mTorr), using electric fields of up to 113 kV/cm. We find induced increases in unimolecular decay rates in 50% of the rotational levels of $\tilde{A}\ ^1A_u$ $v'_3 = 2$ and 3 (v_3' is the number of quanta in the bending mode). We interpret these increases as due to an electric field induced opening of an otherwise symmetry prohibited pathway for dissociation. SAC spectroscopy provides an upper bound for the D^0_0 (H-CCH) 24 kJ/mole lower than that previously inferred [21]. Additional measurements on two lower vibrational levels ($v_2'=1$ and $v_3'=1$) located 8 and 12 kJ/mole below $v3' = 2$ showed no sign of predissociation.

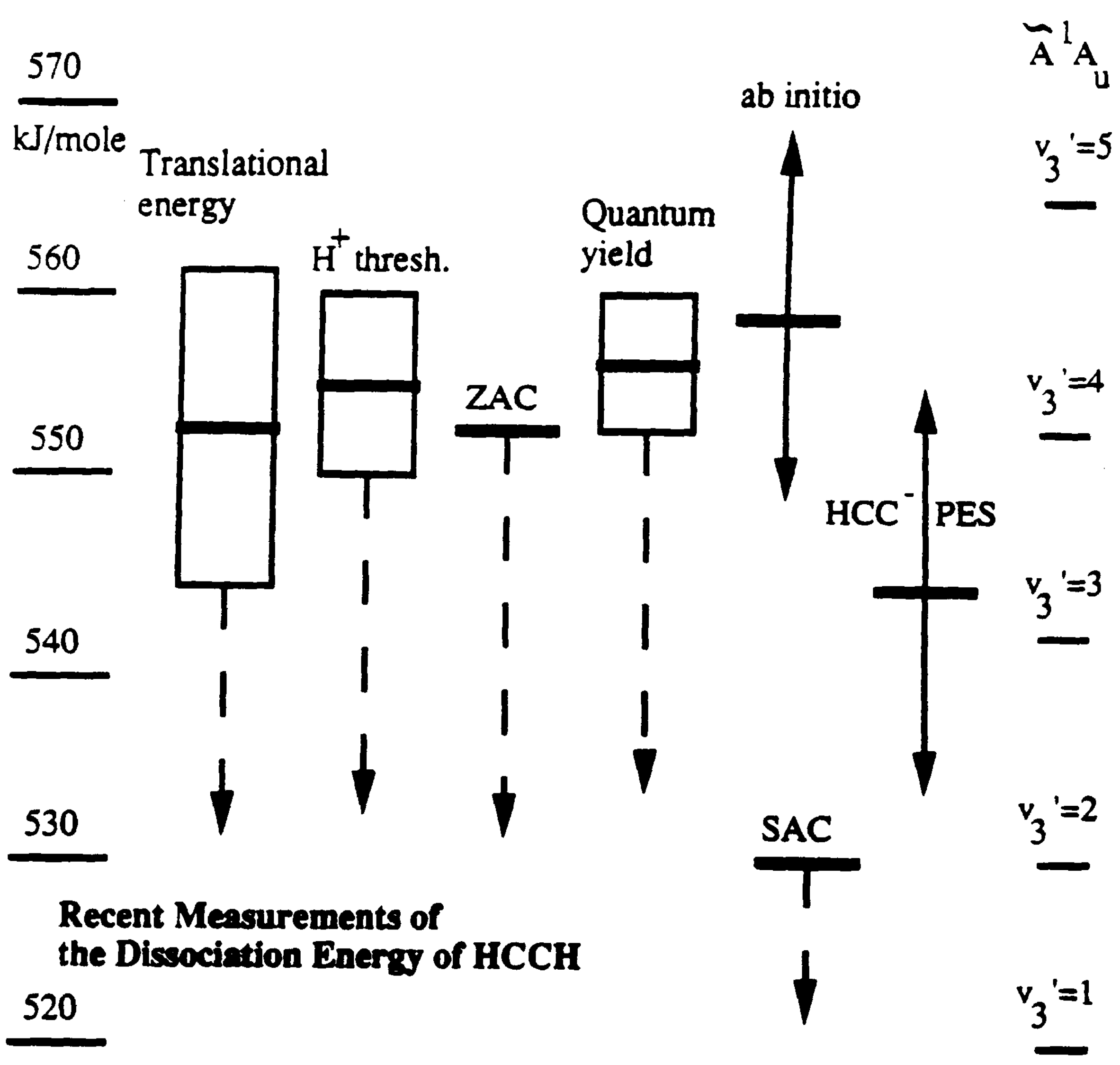

Figure 6: Theoretical calculations and spectroscopic measurements of the CH bond energy in HCCH. Upper bounds are denoted by a dashed downward arrow of unspecifiable length. The cited uncertainty of each measurement in indicated by a box. Note that spectroscopic measurements have very small uncertainties. Thermodynamic measurements and theoretical calculations are denoted by double arrow two sided uncertainties. A recent experiment [26] improves the precision on the upper bound for the appearance energy of CCH$^+$. However, an accurate determination of D^0_0(HCC-H) cannot yet be made from it since the IP(CCH) is not well known.[27,28,29]

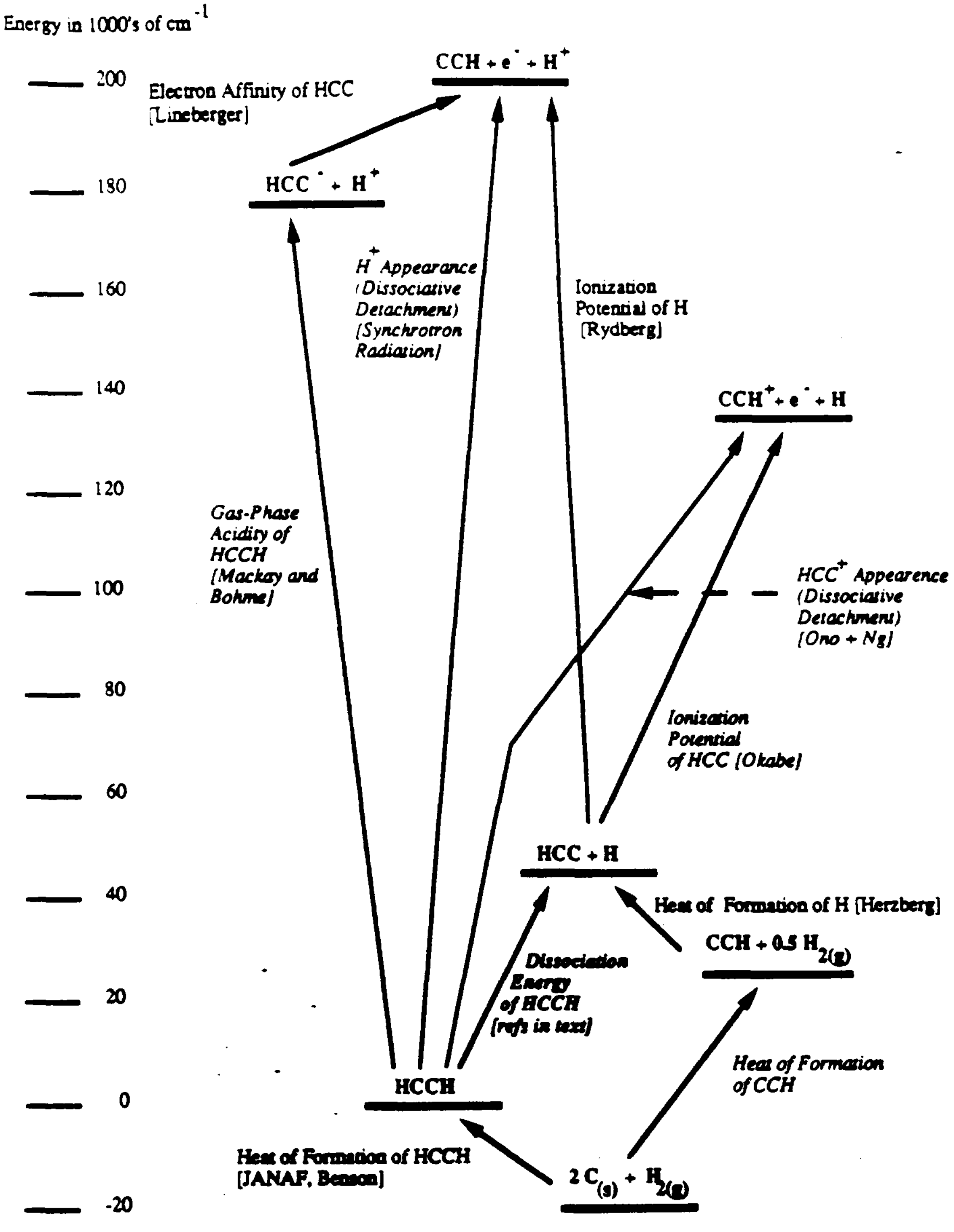

Figure 7: Thermochemistry of Acetylene and related species.

This new evidence for a lower upper bound to D^0_0(HCC-H) is accompanied, however, by other large and as yet unexplained effects.(see Figs. 4 and 5). Each of the 25 rotation-vibration levels studied in detail in the presence and absence of the electric field so far shows not only a change (usually an increase which implies predissociation) in unimolecular decay rate, but also a change in collisional quenching rate and a decrease in the intensity of total detected fluorescence. None of these effects are observed in ZAC Spectroscopy. Thus, the nature of levels with which mixing is induced in SAC vs. ZAC are dramatically different. Although Stark and Zeeman anticrossing spectroscopies are similar techniques for searching among dark states for a weakly predissociated level, the selection rules for perturbations and the behavior of anticrossings are quite different for these two methods.

The result of these experiments is that the upper bound on the CH bond energy is now 2000 cm^{-1} lower than the current consensus value [22-24]. This new value is however in agreement with recent studies modelling acetylene pyrolysis [29,30]. Such a discrepancy in the various methods could be caused by preferential production in other upper bound experiments, of electronically excited CCH (a $^2\Pi$ state lies only 2000-3000 cm^{-1} above the ground $^2\Sigma^+$ state) and/or of vibrationally excited CCH (v_3 = 1 of the C-C stretch). Further work is necessary to understand the discrepancy.

3. LARGE AMPLITUDE MOTION IN ACETLYENE

We have excited acetylene to very high vibrational levels in the ground electronic potential surface using SEP. At energies around 27000 cm^{-1} above the zero point level, the Fourier transform of the SEP spectra exhibits three anomalous recurrences at multiples of 6.5 psec. This energy is well above the barrier to vinylidene⇔◊acetylene isomerization (~15000 cm^{-1}), so that these recurrences are due to a new dynamical motion of the molecule. We have tentatively identified this as large amplitude motions of the hydrogen atoms orbiting around the CC core. By treating the system as a rigid rotor, the analysis of our data suggests a not unreasonable orbital radius of 2.9Å. At present, we have recorded and are analyzing SEP spectra of C_2D_2 in the high energy region in order to determine whether the recurrences have the reduced mass dependence of an internal rotation or a vibration.

In another series of experiments, we have recorded the dispersed fluorescence spectra of HCCH at low and intermediate final energies in the $\tilde{X}\,^1\Sigma_g^+$ state. Between 0 and ~ 10,000cm^{-1} above the zero-point level of the ground state, the features of the fluorescence spectra are easily assignable as progressions in the combination of CC stretching (ν_2'') and trans-bending (ν_4'') modes. Above about 12000 cm^{-1}, the spectrum changes markedly, becoming dominated by a series of "clumps" with a spacing varying monotonically from 1900 cm^{-1} to 1750 cm^{-1}. Each of these are composed of 3 or 4 (depending on energy) smaller clumps (spaced at about ~500cm^{-1}). Finally, these smaller clumps are composed of lines spaced about 10 cm^{-1} apart with a spectrometer-resolution limited width. The composite features can be understood as arising from the short time dynamics of the states populated by the fluorescence (whereby an S_1 vibrational eigenstate is transferred to the S_0 potential energy surface). Since, in the $\tilde{A}^1A_u$ state, the CC bond is lengthened and the molecule becomes trans-bent with respect to the linear $\tilde{X}^1\Sigma_g^+$ ground state, significant Franck-Condon overlap occurs in the regions corresponding to the CC stretch and trans bend distortions in the ground state. The variation in the spacing of the clumps can be thought of as due to the large amplitude bending motion of the hydrogens at high energies, leading to changes in the C-C force constant and effective reduced mass of the core. These motions of the hydrogens can be thought of as precursors of the orbiting motion mentioned above. An obvious follow-up experiment is the measurement of the dispersed fluorescence of the isotopomers of HCCH. We have already recorded dispersed fluorescence spectra of DCCD.

In addition to this experimental work, theoretical work in collaboration with Prof. R. D. Levine of the Hebrew University is underway. Prof. Levine has modelled the potential surface for C_2H_2 and run classical trajectory studies at high energy [31]. He has found some evidence for H orbiting motion as well as fast vibrational energy redistribution. The rates of the fastest redistribution processes match well with rates inferred from the shape of the "correlation" hole in the $<|FT\ I(\omega)|^2>$. We [32] have run similar trajectory studies for isotopically substituted acetylenes in order to assess the effects of such substitutions and symmetry breaking on the dynamics. We found that the energy redistribution rates in $H^{13}C^{12}CH$ are faster than in $H^{12}C^{12}CH$ but slower than in HCCD, as might be expected. We have not seen evidence, in our calculations, for the orbiting motion seen by Levine. Because of uncertainties in the model of the potential surface, we are proceeding cautiously in this theoretical area, remaining as closely coupled to the experiments as possible.

4. EXCITED ELECTRONIC STATES OF ACETYLENE

Single photon electronic transitions are limited to g,u symmetry opposite that of the $\tilde{X}\ {}^1\Sigma_g{}^+$ electronic ground state. UV-optical double resonance allows access to the same g,u symmetry as the ground state while eliminating rotational congestion. Recently, we have observed a vibronic progression (beginning at 62263(10) cm^{-1}) in the C-C stretch mode of the previously unknown trans-bent $\tilde{C}'\,{}^1A_g$ state of both HCCH and DCCD via $\tilde{C}'\,{}^1A_g$ - $\tilde{A}\,{}^1A_u$ - $\tilde{X}\,{}^1\Sigma^+{}_g$ excitation. The fundamental frequencies in both isotopomers were measured: ν_2(HCCH) = 850(20) cm^{-1} and ν_2(DCCD) = 822 cm^{-1}. By varying the intermediate rotational level, we were able to construct term value plots and determine the B rotational constants of the $\tilde{C}$ state to be 0.89 cm^{-1} and 0.70 cm^{-1} respectively. From the spacing of the individual K stacks, values of the A rotational constants were determined to be 7.3 cm^{-1} and 4.85 cm^{-1} respectively. The geometry of this state was also determined, with a C-C bond length of 1.53Å, C-H bond length of 1.27 Å and a CCH bond angle of 68°. Experiments on other g states are planned in the near future.

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