Lester Andrews, Gary P. Kushto, Mingfei Zhou, Stephen P. Willson, and Philip F. Souter

Infrared spectrum of CCH+ in solid argon and neon

Lester Andrews, Gary P. Kushto, Mingfei Zhou, Stephen P. Willson, and Philip F. Souter

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Laser-ablation of over ten different transition, lanthanide, and actinide metals with concurrent codeposition of acetylene/argon samples at 7 K produced metal independent absorptions for CCH, CCH^-, C_4H, and C_4H_2, in agreement with previous matrix isolation work, and a sharp new 1820.4 cm^{-1} band. Isotopic substitution showed this band to be due to a largely C–C stretching mode of a species with one H and two *inequivalent* carbon atoms. The same species were observed in solid neon samples at 4 K, and the neon matrix counterpart of the new band was found at 1832.2 cm^{-1}. When CO_2 was added to serve as an electron trap, the yield of CCH^- at 1772.8 cm^{-1} decreased and the 1832.2 cm^{-1} band increased relative to CCH at 1837.9, 1835.0 cm^{-1}. Quantum chemical calculations at the coupled-cluster and density functional levels predict the C–C stretching mode of CCH^+ between this mode for CCH and CCH^- and support assignment of this new infrared absorption to the CCH^+ cation in solid argon and neon. © *1999 American Institute of Physics.* [S0021-9606(99)01609-8]

I. INTRODUCTION

Laser-ablated transition, lanthanide, and actinide metal atoms have been reacted with acetylene in our laboratory to prepare the M-η^2-C_2H_2 complexes, which are of interest as models for polymerization catalysts.[1–4] In these experiments, several product bands are common to all metal systems, and therefore must be due to hydrocarbon fragments. The most important of these is the ethynyl radical, CCH, which is an intermediate in combustion processes and in the interstellar medium.[5–7] Matrix isolation spectroscopy played an important role in its early detection and characterization.[8–11] Since that time, CCH has been thoroughly studied both in solid matrices and in the gas phase.[12–23] However, much less is known about the charged species CCH^- and CCH^+. Ethynyl anion has been characterized in gas phase electron transfer, photodetachment and photoelectron studies.[24–27] The C–C stretching fundamental of CCH^- has been tentatively identified at 1773.0 cm^{-1} in solid neon,[28] in reasonable agreement with the gas phase 1800 (±20) cm^{-1} measurement.[26] Ethynylium cation has been studied in a number of reactions[29–31] and explored by quantum chemical calculations,[32–38] but only two experimental studies have provided spectroscopic data. Translational energy spectroscopy has reported two broad transitions,[39] and Coulomb explosion imaging has provided evidence for a low frequency bending vibration.[40] It is noteworthy that the Coulomb explosion experimental fit requires a much lower bending frequency than calculated at the Hartree–Fock and MCSCF levels for the bending mode.[35,37]

Laser-ablation has been used in this laboratory to provide energetic metal atoms for reaction with small molecules during condensation in excess argon.[41–48] In studies with O_2, the O_4^- anion is nearly always observed owing to evaporation of electrons from the target surface in the laser-ablation process, and O_4^+ has been detected in some experiments.[41–46] In very recent work with NO, the $(NO)_2^+$ and $(NO)_2^-$ ions were formed and trapped where the laser-induced metal target emission served as a photoionization source.[47] Hence, in addition to metal reaction products, new absorptions common to different metal experiments must be considered for transient species, including molecular ions, derived from the precursor molecule. We report here the first infrared spectrum of CCH^+ in solid argon and neon, from laser-ablated metal studies with acetylene, and quantum chemical calculations on the three similar species CCH^+, CCH, and CCH^- at three levels of theory.

II. EXPERIMENTAL DETAILS

The vacuum system and cryogenic cell for the Nd:YAG laser-ablation-matrix-isolation experiment has been described in detail previously.[41–44] The CsI spectroscopic window was maintained (as measured by a Au/Co vs Chromel thermocouple) by an APD Cryogenics Displex at 7 K or Heliplex at 4 K. Vapor phase metal atoms were produced by focusing the 1064 nm fundamental of a Q-switched Spectra Physics DCR-11 Nd:YAG laser onto rotating Sc, Ti, Zr, Hf, Ce, Pr, Nd, Gd, Yb, Th, and U metal targets (Johnson Matthey and Oak Ridge National Laboratory). The average laser pulse duration was 10 ns and the laser energy at the target was varied between 5 and 50 mJ/pulse with a 10 Hz repetition rate.

The acetylene samples (0.5%–0.1% in argon or neon) were codeposited 1–2 h at 3–5 mmol/h with laser-ablated metal. Isotopically labeled samples ($^{13}C_2H_2$, C_2D_2 and 3:5:2 statistically scrambled HCCH:DCCH:DCCD) were also prepared to elucidate the effects of isotopic substitution on the vibrational spectra of the reaction products.

Infrared spectra were recorded on a Nicolet 550 or 750 spectrometer bench operating with a spectral resolution of 0.5 cm^{-1} and a frequency accuracy of 0.1 cm^{-1}. Spectra were collected at the end of each deposition and before and after annealings or photolyses. Typically, each argon matrix was annealed quickly to 25 K, 35 K, 40 K, and 45 K and each neon matrix to 7, 9, and 11 K. Broadband mercury arc photolysis using a medium pressure mercury arc lamp (Phil-

ips H39KB) with the outside globe removed were performed at several different points in the course of the experiments in order to evaluate the photosensitivity of different product species and to aid in spectral interpretation.

III. COMPUTATIONAL METHODS

Quantum chemical calculations were performed on selected acetylene fragments for the present work using the GAUSSIAN 94 suite of programs.[49] Calculations on the CCH radical, CCH^+ triplet, and CCH^- singlet species were completed using post-Hartree–Fock *ab initio* as well as hybrid and pure density functional (DFT) methods. For the pure density functional approach, the exchange and correlation functionals of Becke[50] and Perdew[51] (BP86), were used while the three-parameter hybrid functional according to Becke[52] with additional correlation corrections due to Lee, Yang, and Parr[53] were utilized in the DFT/*ab initio* hybrid approach (B3LYP). In the BP86 and B3LYP calculations, both the carbon and hydrogen atoms were described using the typical 6-31+G**, double ζ quality basis sets included in the GAUSSIAN 94 program. The coupled cluster approach with inclusion of single, double and iterative inclusion of triple excitations (CCSD(T)) from the Hartree–Fock determinant was applied to the simple acetylene fragments. In the CCSD(T) calculations, the augmented, correlation consistent, valence double ζ basis sets (aug-cc-pVDZ) formulated by Woon and Dunning[54] were used to describe the carbon and hydrogen atoms. All vibrational frequencies produced at this level of theory were determined by numerical evaluation of the second derivatives of the molecular potential energy surfaces while those at the BP86 and B3LYP levels were determined by analytical solution of the molecular Hessian matrix.

IV. RESULTS

Infrared spectra of selected laser-ablated metal and acetylene systems will be reported in solid argon and solid neon followed by calculated parameters for acetylene and fragments.

A. Solid argon

Three bands of primary importance were observed at 1845.8, 1820.4, and 1770.5 cm^{-1} with normal isotopic acetylene unshifted in over ten different metal experiments. The 1820.4 cm^{-1} band was always accompanied by a weaker satellite at 1813.5 cm^{-1}. The 1845.8 cm^{-1} band and isotopic modifications are in excellent agreement with absorptions reported by Jacox *et al.* for CCH radical [9–11] and the sharp 1770.5 cm^{-1} absorption matches the band tentatively assigned by Jacox and co-workers[28] to CCH^- in solid argon. In addition, the strongest absorptions of the C_4H radical at 2060.4 cm^{-1} and of C_4H_2 at 3325.4, 627.5 cm^{-1} were observed.[55–57] With a uranium target, the strongest $C_2H_2^+$ band was observed at 3104.4 cm^{-1}, again in agreement with Jacox *et al.*[28] Table I collects the metal-independent argon matrix product absorptions.

Figure 1 shows spectra for uranium after deposition, annealing, photolysis, and further annealing. Each annealing

TABLE I. Metal independent absorptions (cm^{-1}) observed in laser-ablated metal experiments with acetylene in solid argon at 7 K.

C_2H_2	$^{13}C_2H_2$	C_2D_2	Assignment
3325.4	3308.8	2593.0	C_4H_2
3318.5	3302.6	$\cdots$	CCH^-
$\cdots$	$\cdots$	2496.0	CCD^+
3104.4	3095.0	2311.5	$C_2H_2^+$
2084.0	2005.7	2056.5	C_xH_y
2060.4	1981.5	2049.4	C_4H
$\cdots$	1819.9	$\cdots$	$^{13}C^{12}CH$
$\cdots$	1812.3	$\cdots$	$^{12}C^{13}CH$
1845.8	1785.5	1746.5	CCH
$\cdots$	1791.1	$\cdots$	$^{13}C^{12}CH^+$
1820.4	1755.1	1724.6	CCH^+
1813.5	1748.6	1715.8	CCH^+ site
$\cdots$	1715.2	$\cdots$	$^{13}C^{13}CH^-$ site
1770.5	1711.8	1676.7	CCH^-
549.5	544.8	433.8	CCH^+

cycle slightly decreased the subject product absorptions. Broadband photolysis *decreased* the 1845.8 and 1770.5 cm^{-1} bands by 10%, *increased* the 1820.4 cm^{-1} band by 10%, and *decreased* the 3104.4 cm^{-1} band by 50%. The same photolysis behavior was found in the higher laser power transition metal experiments, whereas in the lower power transition and lanthanide metal studies these four bands slightly decreased on photolysis.

Experiments with $^{13}C_2H_2$ shifted the three primary bands to 1785.6, 1755.1, and 1711.8 cm^{-1}. Since this sample contained 14% $H^{13}C^{12}CH$, two weaker bands were observed at 1819.9 and 1812.3 cm^{-1} for $^{12}C^{13}CH$ and $^{13}C^{12}CH$ with $\frac{1}{12}$ of the 1785.6 cm^{-1} band intensity, and a sharp, weak 1791.1 cm^{-1} counterpart was observed for the 1755.1 cm^{-1} band with $\frac{1}{12}$ of the intensity of the 1755.1 cm^{-1} absorption.

Investigations with C_2D_2 gave primary bands at 1746.5, 1724.6, and 1676.7 cm^{-1}. Figures 2, 3, and 4 contrast spectra for the three isotopic precursors after sample deposition at 7 K using Ti, Yb, and U targets, respectively. Note that the Yb spectra with C_2H_2 are similar to the U spectra, but the Ti spectra give enhanced yields of the new 1820.4 cm^{-1} product absorption. Spectra with Zr and Hf were more like Yb spectra in product population.

One experiment performed with a mixed C_2H_2, HC$_2$D, C_2D_2 sample and Sc gave only the product bands described above for C_2H_2 and C_2D_2.

B. Solid neon

Experiments were performed with Ti and Sc and acetylene in neon on a 4 K substrate, and a typical spectrum is shown in Fig. 5. Bands were observed at 1837.9, 1835.0, and 1832.2 cm^{-1}, in very good agreement with the 1838.1, 1835.5, 1832.3 cm^{-1} trio assigned by Jacox and co-workers[23] to CCH in solid neon. However, the 1832.2 cm^{-1} band is stronger in our experiments and it decreases on photolysis while the 1837.9 and 1835.0 cm^{-1} bands increase. In addition, a strong, sharp photosensitive band at 1772.8
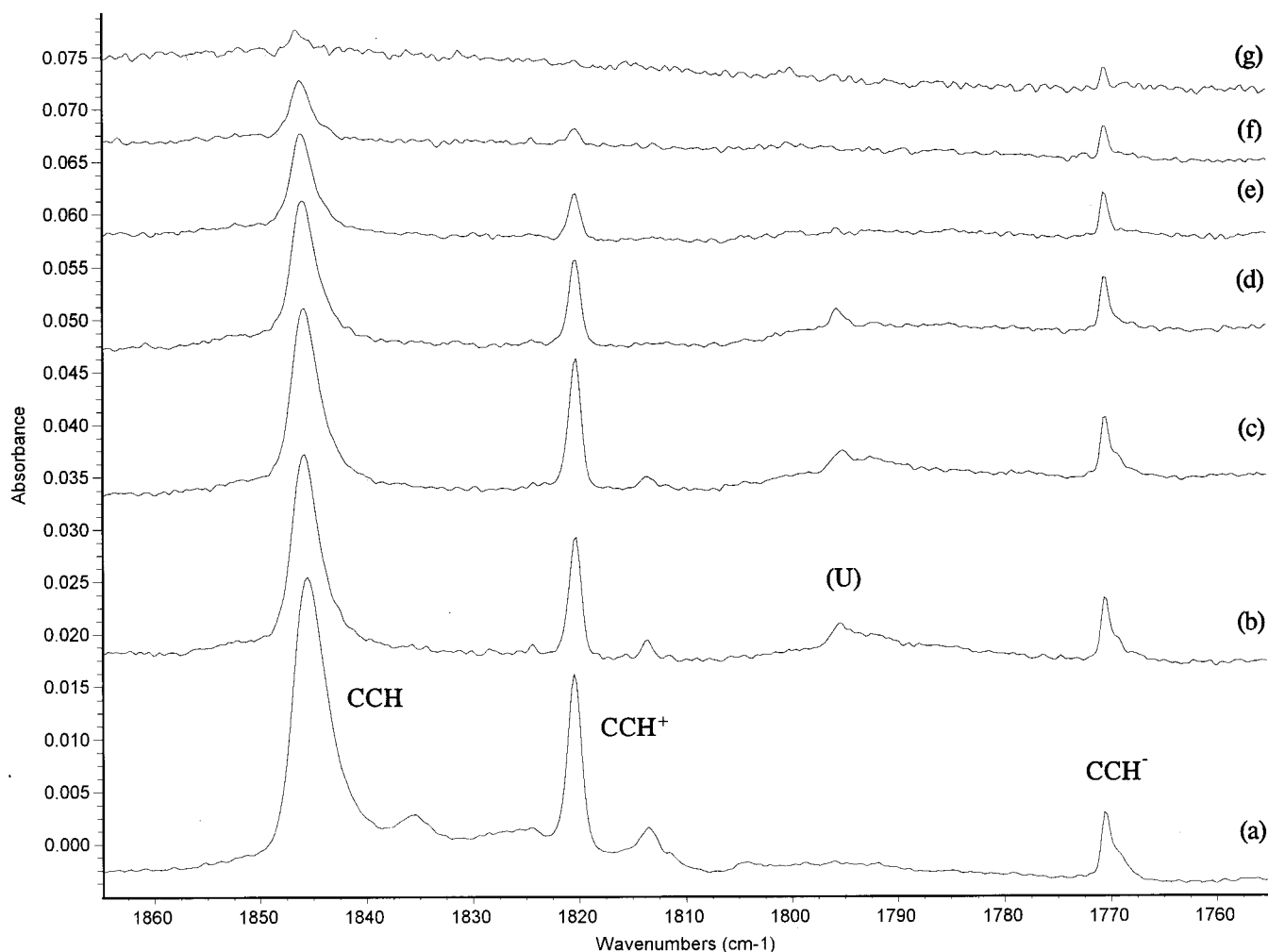
FIG. 1. Infrared spectra in the 1865–1755 cm^{-1} C–C stretching region for laser-ablated U atoms codeposited with argon; $^{12}C_2H_2$ (300:1) sample at 7 K. (a) Following 2 h of codeposition, (b) matrix annealed to 22 K, (c) following 30 min broadband Hg arc photolysis, (d) matrix annealed to 27 K, (e) matrix annealed to 34 K, (f) matrix annealed to 38 K, and (g) matrix annealed to 42 K. The band labeled (U) is metal dependent.

cm^{-1} is in excellent agreement with the 1773.0 cm^{-1} band tentatively assigned previously to the CCH$^-$ anion.[28] Annealing cycles decrease the upper bands in favor of the 1837.9 cm^{-1} site, decrease the 1832.2 and 1772.8 cm^{-1} absorptions, and produce a weak C$_4$H$_2$ absorption at 3316.5 cm^{-1}.[23,57]

Two investigations were done with CO$_2$ added to serve as an electron trap,[58] and a spectrum is compared in Fig. 5(d). Note that the 1832.2 cm^{-1} band is *increased* and the 1772.8 cm^{-1} band is *decreased* relative to the 1835.0 cm^{-1} CCH radical band and that CO$_2^-$ species are observed at 1658.1 and 1665.2 cm^{-1}, in agreement with observations of CO$_2^-$ from the Jacox laboratory.[59] Photolysis ($\lambda > 290$ nm) destroyed the CO$_2^-$ bands, decreased the new 1832.2 cm^{-1} band and slightly *increased* the 1772.8 cm^{-1} feature. Further full arc photolysis increased CCH absorption at the expense of both 1832.2 and 1772.8 cm^{-1} absorptions, Fig. 5(g).

Two investigations were done with the $^{13}C_2H_2$ sample containing a trace of CO$_2$ impurity. The initial spectrum revealed sharp, weak bands at 1778.8 and 1775.8 cm^{-1}, in excellent agreement with the bands for $^{13}C^{13}CH$ in solid neon,[23] plus new stronger bands at 1767.6 and 1716.7 cm^{-1}, with a blue shoulder at 1719.4 cm^{-1}, and CO$_2^-$ at 1658.1 cm^{-1} with a satellite at 1665.2 cm^{-1}, as shown in Fig. 6(a). Photolysis with $\lambda > 290$ nm almost destroyed the CO$_2^-$ bands and slightly decreased the 1767.6 and 1716.7 cm^{-1} features, and continued irradiation with the full arc *decreased* these bands further, *increased* the 1778.8 and 1775.8 cm^{-1} bands, and resolved another 1773.2 cm^{-1} feature. Annealing to 7 K coalesced the upper bands into a single 1778.8 cm^{-1} site, decreased the 1767.6 cm^{-1} band and 1719.4 cm^{-1} shoulder, and produced Ti dependent features at 1693.5 and 1665.4 cm^{-1}.

Two experiments were performed with C$_2$D$_2$, and the initial spectrum, Fig. 6(e), revealed an absorption at 1739.9 cm^{-1}, in agreement with Jacox *et al.*[23] for CCD, and stronger new bands at 1735.1 and 1675.7 cm^{-1}. Annealing to 6 K increased the CCD band, and full arc photolysis decreased the latter new bands and increased the CCD band, Fig. 6(g). A final 9 K annealing slightly sharpened the bands. Table II summarizes the metal-independent neon matrix product absorptions.
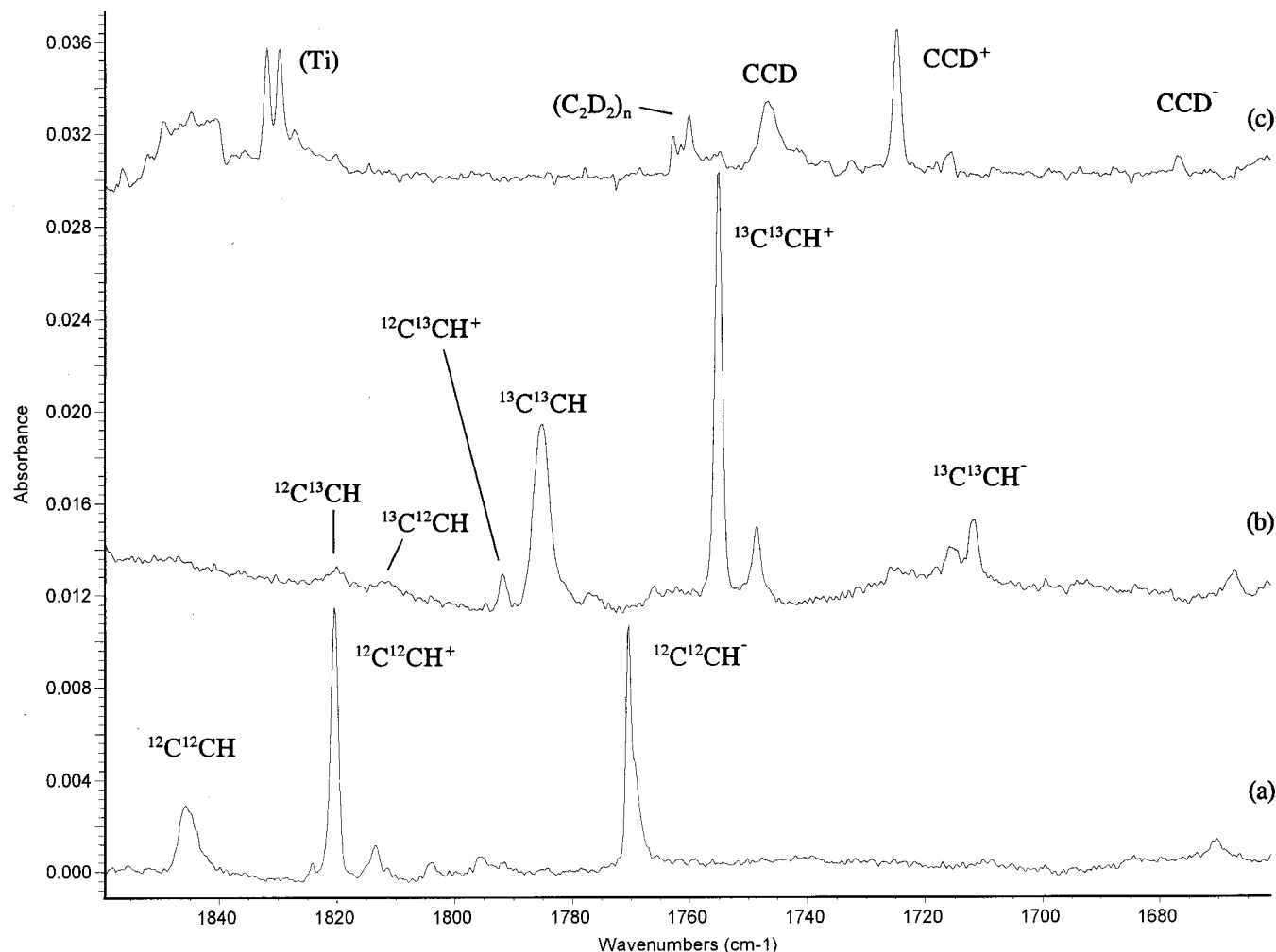
FIG. 2. Infrared spectra in the 1860–1660 cm^{-1} C–C stretching region of the reaction products of laser-ablated Ti atoms with argon: acetylene (200:1) samples. (a) $^{12}C_2H_2$, (b) $^{13}C_2H_2$, and (c) $^{12}C_2D_2$. All spectra were collected of matrices directly following 1–2 h of codeposition at 7 K. The band labeled (Ti) is metal dependent.

C. Calculations

The present calculations predict that $^2\Sigma$ is the ground state for CCH radical, in agreement with previous investigations;[36,60] however, an interesting dicotomy between DFT and *ab initio* based methods is found. In the CCSD(T) calculations, the linear, $^2\Sigma$ state produces vibrational frequencies at 3430, 2019, and 207 cm^{-1}, which are in reasonable agreement with the experimentally observed spectrum,[23] except for the low-frequency bending mode.[23] In the pure DFT/BP86 calculations, vibrational normal modes are predicted at 3395, 2021, and −676 cm^{-1}, which obviously indicate that on the BP86 potential, the CCH radical is bent, a result incompatible with all experimental evidence. Although BP86 calculations on a bent CCH frame remove the negative bending coordinate, the vibrational frequencies produced by this structure are significantly perturbed from those expected for this species, indicating the complete inability of this method to model the CCH system (see Table III).

In addition to the two above mentioned calculations, a third computational approach was applied to the CCH radical to determine the applicability of a hybrid DFT functional to this difficult problem. The B3LYP functional produced all positive vibrational frequencies for the linear structure indicating that the Hartree–Fock portion of the B3LYP functional provides the important information needed to correctly describe the geometry of the ethynyl radical. The B3LYP functional produces a primarily C–C stretching fundamental at 2048 cm^{-1} which is in reasonable agreement with the CCSD(T) value listed above as well as with the experimentally observed value. Regardless of the method applied, it is obvious that the overestimation of the vibrational frequency of the C–C stretching coordinate is an artifact of the inability of any of the computational methods used here to deal with the multiconfigurational nature of the CCH molecular wave function.

Similar calculations were performed on C_2H_2 as a calibration, and on the charged fragments CCH$^+$ and CCH$^-$. Results are summarized in Table III.

V. DISCUSSION

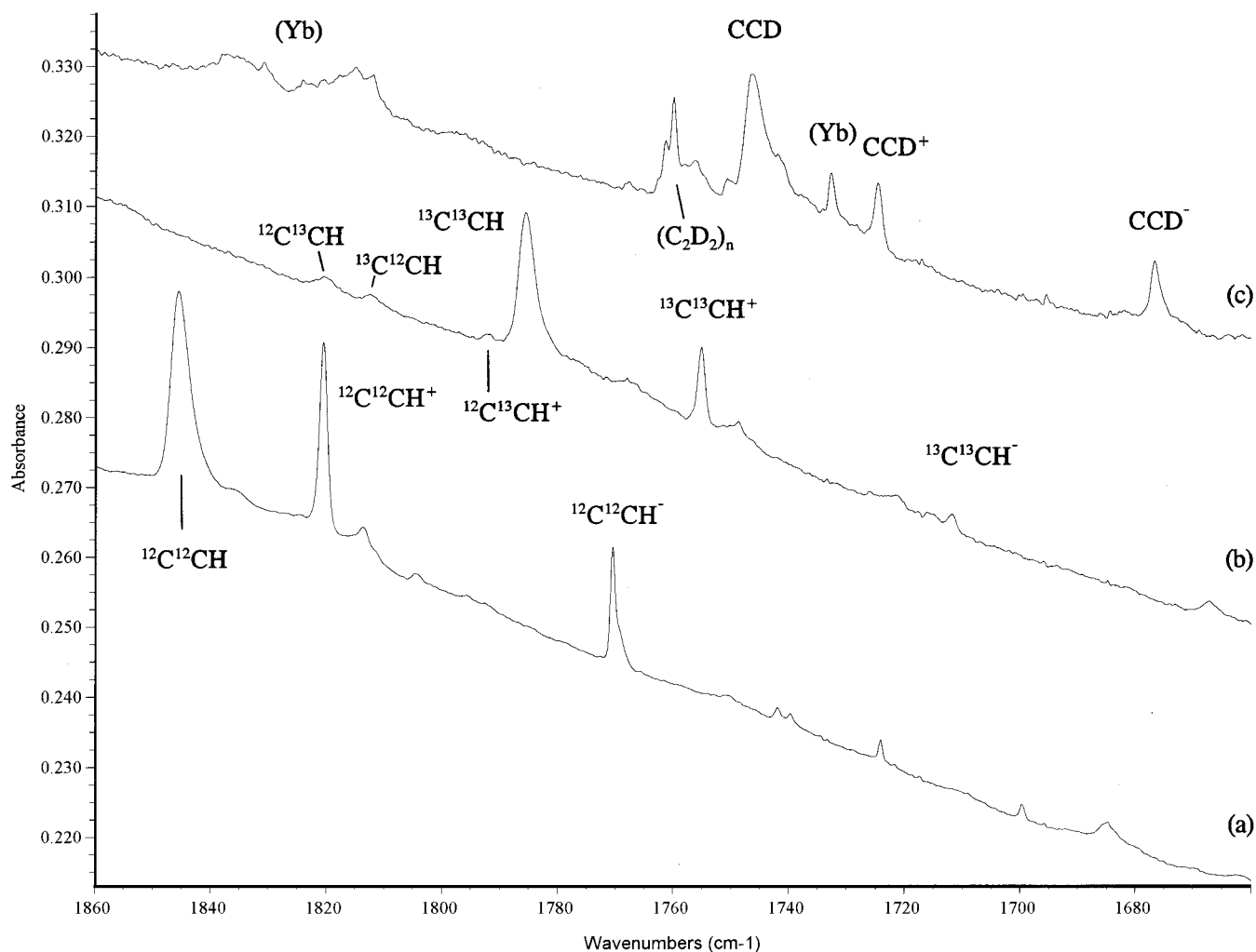The new infrared absorptions at 1820.4 cm^{-1} in solid argon and 1832.2 cm^{-1} in solid neon will be assigned to the

FIG. 3. Infrared spectra in the 1860–1660 cm^{-1} C–C stretching region of the reaction products of laser-ablated Yb atoms with argon: acetylene (200:1) samples. (a) $^{12}C_2H_2$, (b) $^{13}C_2H_2$, and (c) $^{12}C_2D_2$. All spectra were collected of matrices directly following 1–2 h of codeposition at 7 K. The band labeled (Yb) is metal dependent.

CCH$^+$ cation with the help of isotopic substitution, mechanical modeling with CCH, and quantum chemical calculations.

A. CCH

Previous matrix and gas phase spectroscopy show that the 1845.8 cm^{-1} ($^{12}C^{12}CH$) and 1785.5 cm^{-1} ($^{13}C^{13}CH$) bands are due to the ethynyl radical.[9,11,12,14,28] This species is discussed here as a stoichiometric precursor for CCH$^-$ and CCH$^+$. Although the 1845.8 cm^{-1} absorption appears in the C–C triple bond stretching region, the deviation of the $^{12}C/^{13}C$ isotope ratio of this mode (1.033 77) from that of the C–C harmonic value (1.040 97) suggests that this vibration is coupled to the C–H motions of this molecule. The contribution of the C–H stretching vibrations to this mode is borne out by the H/D isotope ratio (1.056 86) and 99.3 cm^{-1} red shift exhibited by this band upon deuteration of the acetylene precursor. The identification as CCH is further characterized by the spectrum with 92.5% carbon-13 enriched acetylene, which contains 86% $^{13}C_2H_2$ and 14% H$^{12}C^{13}CH$. Three isotopic products are observed in this experiment at 1819.9, 1812.3, and 1785.6 cm^{-1} [in a 1:1:12 relative intensity, see

Fig. 2(b)] for the $^{12}C^{13}CH$, $^{13}C^{12}CH$, and $^{13}C^{13}CH$ radicals, which is in agreement with previous assignments.[12,28]

B. CCH$^-$

In addition to the ethynyl radical, two additional species are formed as a result of heterolytic cleavage of the acetylenic C–H bond. The band at 1770.5 cm^{-1} in argon and at 1772.8 cm^{-1} in neon experiments is due to the primarily C–C stretching motion of the CCH$^-$ anion based on isotopic behavior as well as by analogy with previous matrix isolation experiments. Jacox *et al.* assigned bands at 1773.0 cm^{-1} in solid neon and 1770.7 cm^{-1} in solid argon[28] to the C–C stretching fundamental of the CCH$^-$ anion based on comparison of their matrix spectra with the gas-phase photoelectron data collected on this species by Ervin and Lineberger.[26] Unfortunately, in neither of the previous matrix studies were counterparts for the latter absorptions observed in the $^{13}C_2H_2$ or C$_2$D$_2$ experiments making an unambiguous assignment of this species difficult; however, in the H$^{12}C^{13}CH$ experiments in neon, the appearance of bands at 1773.0, 1755.8, and 1733.6 cm^{-1} were attributed to the first three members of a
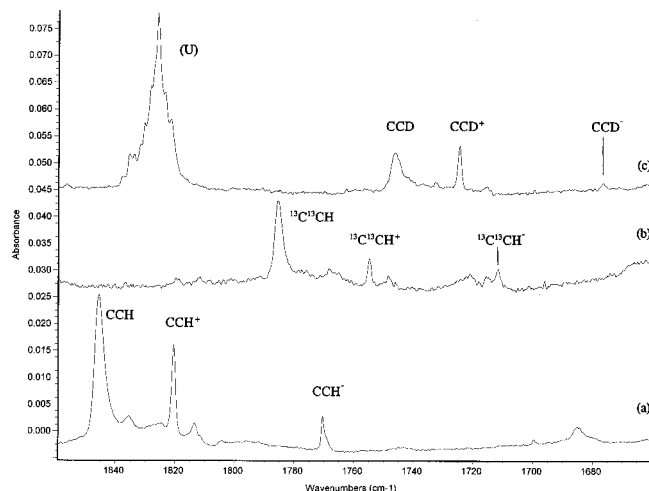
FIG. 4. Infrared spectra in the 1860–1660 cm^{-1} C–C stretching region of the reaction products of laser-ablated U atoms with argon: acetylene (300:1) samples. (a) $^{12}C_2H_2$, (b) $^{13}C_2H_2$, and (c) $^{12}C_2D_2$. All spectra were collected of matrices directly following 2 h of codeposition at 7 K. The band labeled (U) is metal dependent.

FIG. 6. Infrared spectra in the 1790–1650 cm^{-1} region for neon: isotopic acetylene samples codeposited with laser-ablated Ti atoms at 4 K. (a) 0.5% $^{13}C_2H_2$ and 0.01% CO_2 codeposited for 1 h, (b) after photolysis λ >290 nm for 20 min, (c) after full arc photolysis for 20 min, (d) after annealing to 7 K, (e) 0.25% C_2D_2 codeposited for 1 h, (f) after 6 K annealing, (g) after full arc photolysis for 20 min, and (h) after 9 K annealing. The band labeled I is an impurity in the sample.

carbon isotopic quartet providing evidence that this vibration is likely due to a species containing two inequivalent carbon atoms. In addition, the C–C stretching fundamental for CCH$^-$ measured at 1800±20 cm^{-1} in the photoelectron spectrum further supported the latter assignment once matrix shift effects on the vibrational frequency are taken into account.[26,28]

In the present argon matrix work, the spectra of metal reactions with acetylene produce a band at 1770.5 cm^{-1}, which is due to the primarily C–C stretching mode of the CCH$^-$ anion. This is in agreement with the earlier assignment;[28] however, the present results provide further support. In the $^{13}C_2H_2$ experiments, the weaker band at 1711.8 cm^{-1} can be identified as the $^{13}C^{13}CH^-$ counterpart

of the 1770.5 cm^{-1} $^{12}C^{12}CH^-$ frequency, which was not observed in the previous reports. The large $^{12}C/^{13}C$ isotope ratio produced by this mode (1.034 29) is certainly consistent with a C–C stretching mode when compared with the analogous value obtained for the CCH species above. In addition, the C_2D_2 experiments produce a weak absorption at 1676.7 cm^{-1}, which can be assigned to the CCD counterpart of this vibration. The 93.6 cm^{-1} red shift upon deuteration produces a 1.055 94 H/D ratio, which is once again very similar to the value exhibited by the radical species, further supporting the previous and present matrix assignments.

In addition to the absorption due to the primarily C–C stretching mode, a weak absorption at 3318.5 cm^{-1} can be attributed to the C–H vibration of the anion based on photolysis and annealing behavior. This weak feature appears as a sharp satellite on the red side of the much more intense absorption at 3326.1 cm^{-1} due to the C–H stretch of diacetylene.[57] This feature shifts to 3302.6 cm^{-1} in the $^{13}C_2H_2$ experiments producing a 1.004 81 $^{12}C/^{13}C$ isotope ratio, which is in excellent agreement with the 1.004 79 ratio predicted by the CCSD(T) calculations. Unfortunately, the perdeutero counterpart of these absorptions is not observed in the C_2D_2 experiments, most likely due to the poor yield of this species.
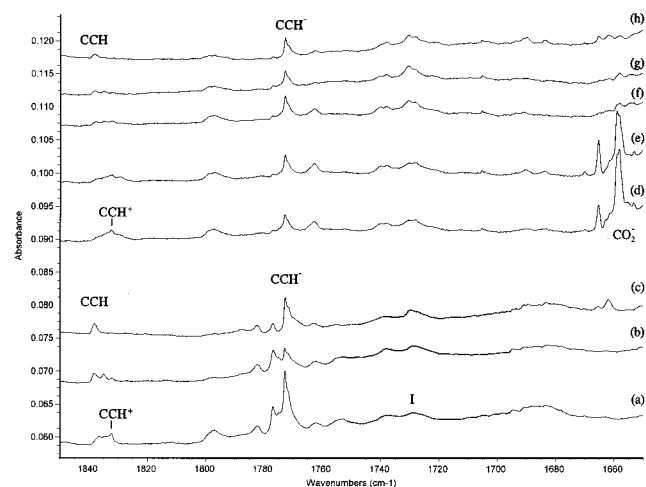

FIG. 5. Infrared spectra in the 1850–1650 cm^{-1} region for neon: C_2H_2 samples codeposited with laser-ablated Ti atoms at 4 K. (a) 0.5% C_2H_2 in neon codeposited for 1 h, (b) after full arc photolysis for 20 min, (c) after annealing to 11 K, (d) 0.25% C_2H_2 and 0.05% CO_2 in neon codeposited for 1 h, (e) after annealing to 7 K, (f) after photolysis λ >290 nm for 20 min, (g) after full arc photolysis for 20 min, and (h) after annealing to 11 K. The band labeled I is acetone impurity in the sample.
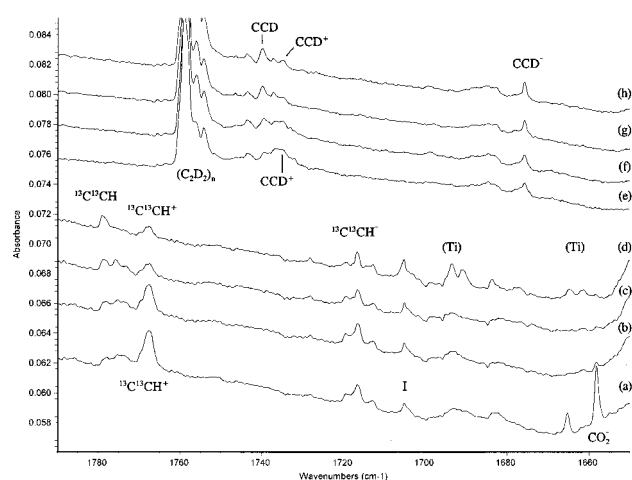
TABLE II. Metal independent absorptions (cm^{-1}) observed in laser-ablated metal experiments with acetylene in solid neon at 4 K.

C_2H_2	$^{13}C_2H_2$	C_2D_2	Assignment
3135	3125	2327	$C_2H_2^+$
2086.7	⋯	⋯	C_xH_y
2063.7	1984.7	2052.5	C_4H
1837.9	1778.7	1739.9	CCH
1835.0	1775.9	1737.2	CCH
1832.2	1767.6	1735.1	CCH$^+$
1772.8	1716.7	1675.7	CCH$^-$

TABLE III. *Ab initio* [CCSD(T)/aug-cc-pVDZ], density functional (BP86/6-31+G**) and hybrid (B3LYP/6-31+G**) energies (a.u.), harmonic vibrational frequencies (cm^{-1}), intensities (km/mol), and bond lengths (Å) for acetylene and the fragments CCH, CCH$^+$, and CCH$^-$.

Species	State	Energies	Frequencies (Intensities)	Bond lengths
			CCSD(T)	
HCCH	$^1\Sigma_g^+$	−77.121 38	σ_g 3479, σ_u 3385, σ_g 1969, π_u 691, π_g 367[a]	1.2301, 1.0787[b]
CCH	$^2\Sigma^+$	−76.408 94	σ 3430, σ 2019, π 207	1.2329, 1.0795
CCH$^+$	$^3\Pi$	−75.993 67	σ 3247, σ 1831, π 747, π 201	1.2802, 1.0990
CCH$^-$	$^1\Sigma^+$	−76.515 99	σ 3313, σ 1786, π 397	1.2763, 1.0878
			BP86	
HCCH	$^1\Sigma_g^+$	−77.327 93	σ_g 3456(0), σ_u 3361(85), σ_g 2004(0), π_u 734(113), π_g 536(0)	1.2192, 1.0743
CCH ($C_{\infty v}$)	$^2\Sigma^+$	−76.605 33	σ 3395(57), σ 2021(5), π −676(156×2)	1.2231, 1.0759
CCH (C_s)	$^2A'$	−76.606 74	a' 3288(13), a' 1554(639), a' 604(56)	1.2505, 1.0854
CCH$^+$	$^3\Pi$	−76.182 17	σ 3207(254), σ 1834(12), π 745(24), π 129(1)	1.2713, 1.0964
CCH$^-$	$^1\Sigma^+$	−76.722 08	σ 3276(11), σ 1812(91), π 514(158×2)	1.2643, 1.0829
			B3LYP	
HCCH	$^1\Sigma_g^+$	−77.335 49	σ_g 3533(0), σ_u 3435(94), σ_g 2068(0), π_u 770(114), π_g 611(0)	1.2081, 1.0664
CCH	$^2\Sigma^+$	−76.611 00	σ 3333(59), σ 2048(8), π 165(44×2)	1.2173, 1.0825
CCH$^+$	$^3\Pi$	−76.189 98	σ 3284(256), σ 1902(13), π 782(21), π435(6)	1.2586, 1.0878
CCH$^-$	$^1\Sigma^+$	−76.722 08	σ 3275(11), σ 1813(91), π 514(158×2)	1.2642, 1.0830

[a]Observed values in order 3374, 3287, 1974, 729, and 612 cm^{-1}; G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, New York, 1945).
[b]The first (longer) bond is C–C, and the second (shorter) bond is C–H.

The present neon experiments gave a strong, sharp $^{12}C^{12}CH^-$ band at 1772.8 cm^{-1}. In addition, neon matrix $^{13}C^{13}CH^-$ and CCD$^-$ bands were observed here at 1716.7 and 1675.7 cm^{-1}. The 12/13 (1.032 68) and H/D (1.057 95) ratios for these modes in solid neon are in reasonable agreement with the above solid argon ratios suggesting that the normal modes are not matrix dependent.

Calculations on the CCH$^-$ anion provide further support for the present assignment with CCSD(T) calculations predicting vibrational frequencies for the anion at 3313, 1786, and 397 cm^{-1}. Unlike the radical species described above, both the BP86 and the B3LYP computational approaches describe the anion well and predict vibrational frequencies very similar to those produced by the coupled-cluster results.

C. CCH$^+$

In contrast with the earlier matrix experiments on the fragmentation and ionization of acetylene by Jacox *et al.*,[23,28] the present matrix reactions produce a prominent band at 1820.4 cm^{-1}, which is a candidate for assignment to the ethynylium cation, CCH$^+$. Although a weak band at 1820.8 cm^{-1} was listed in tables, no assignment was made.[23,28] This absorption appears between the analogous modes for CCH and CCH$^-$, as predicted by the CCSD(T) calculations, and exhibits slightly different isotopic frequency ratios than those of the above species. In the metal experiments with $^{13}C_2H_2$, this band shifts to 1755.1 cm^{-1} producing a $^{12}C/^{13}C$ ratio of 1.037 21, which is slightly larger than that exhibited by the C–C stretching modes of the CCH and CCH$^-$ acetylene

fragments. In a complementary fashion, this mode exhibits an H/D ratio of 1.055 49, which is slightly smaller than that in the neutral radical or molecular anion.

In the carbon-13 experiments, a sharp, weak 1791.9 cm^{-1} absorption tracks with the sharp, 1755.1 cm^{-1} all carbon-13 band on annealing and photolysis (Figs. 2, 3, 4). All three of the calculations performed here predict the $^{12}C^{13}CH^+$ isotopic modification to occur 28.8±0.5 cm^{-1} below the carbon-12 species, and the 1791.9 cm^{-1} band is in perfect agreement at 28.5 cm^{-1} below the proposed $^{12}C^{12}CH^+$ absorption; furthermore, the 1791.9 cm^{-1} band is $\frac{1}{12}$ of the intensity of the 1755.1 cm^{-1} band, which is in agreement with the statistical weights of the isotopic reagent as mentioned above. Unfortunately, the $^{13}C^{12}CH^+$ isotopic species is expected to absorb another 8.3 cm^{-1} lower in frequency and is marked by the strong $^{13}C^{13}CH$ radical band at 1785.5 cm^{-1}. The weak 1791.9 cm^{-1} feature shows that this absorption is produced by a species that contains two symmetry *inequivalent* carbon atoms much like the CCH radical discussed above. With C$_2$D$_2$ the counterpart shifts to 1724.6 cm^{-1}, an amount (95.8 cm^{-1}) appropriate for a C–C stretching mode interacting with a *single* H (or D) atom.

The new 1832.2 cm^{-1} band in solid neon decreases on photolysis along with the CCH$^-$ band, as is appropriate for CCH$^+$, while the 1837.9 cm^{-1} CCH radical band increases. Furthermore, the presence of the CO$_2$ molecule to trap electrons *reduces* CCH$^-$ and *increases* the new 1832.2 cm^{-1} CCH$^+$ band relative to the CCH band. The 12/13 (1.03655) and H/D (1.05596) ratios are in excellent agreement with the above argon matrix counterpart isotopic ratios.

The 1820.4 cm^{-1} argon matrix band is assigned here to the C–C stretching mode of CCH$^+$. The weak 1820.8 cm^{-1} band in previous argon discharge experiments[23,28] is assigned likewise. The 1832.2 cm^{-1} counterpart band is assigned to CCH$^+$ in solid neon.

In addition to the band at 1724.6 cm^{-1} in the argon/C$_2$D$_2$ experiments, a weak feature at 2496.1 cm^{-1} about 20% as intense can be assigned to the primarily C–D stretching mode of the CCD$^+$ cation. In the C$_2$H$_2$ and ^{13}C$_2$H$_2$ experiments, this vibration is coincident with one of the partners of the Fermi-doublet due to the acetylene precursor, and is unobserved. In the C$_2$D$_2$ experiments, this vibration undergoes a smaller shift than the associated acetylene mode, moving this feature into a less congested region of the spectrum.

Different mixing of the C–C and C–H coordinates of this species suggests that there may be unusual electronic effects occurring in the cation that are not present in the other acetylene fragments investigated herein. One such electronic effect is the Renner–Teller (R–T) coupling that splits the bending mode energy levels of the linear $^3\Pi$ cation.[61] Although no calculation has accurately predicted the bending mode absorption spectrum for CCH$^+$, more than one transition might be observable. The Coulomb explosion experiments[40] suggest a bending frequency near 200 cm^{-1}. Such a mode is well below the spectral region of our spectrometer, but it is conceivable that a higher energy component may be observed in the present spectra. By noting that the photolysis and annealing behaviors of the argon matrix band at 549.5 cm^{-1} are identical to those of the feature at 1820.4 cm^{-1}, it is reasonable to assign 549.5 cm^{-1} as one component of the R–T split H–C–C bending mode of the CCH$^+$ cation. The large H/D ratio of 1.266 71 and relatively small ^{12}C/^{13}C ratio of 1.008 63 for this mode are consistent with a H–C–C bending mode. The 549.5 cm^{-1} absorption tracks with the 1820.4 cm^{-1} band in all experiments and the assignment of the associated bending mode further supports this identification of CCH$^+$.

These experimental isotopic ratios are in excellent agreement with those predicted for the higher frequency component of this R–T doublet by the quantum mechanical calculations [CCSD(T) results produce H/D = 1.260 95 and ^{12}C/^{13}C = 1.010 07]; however it must be kept in mind that the calculations may have an error associated with the forms of the calculated bending modes of this species as a result of the Renner–Teller effect. Nonetheless, the calculations help to support the current assignment.

The calculated frequencies of the C–C stretching vibrations of CCH, CCH$^+$, and CCH$^-$ suggest that these vibrations fall in this order in the infrared spectrum. All of the calculations included herein, regardless of the level of theory applied, suggest that the ethynyl radical should have the highest frequency C–C stretching vibration, with the cation in the middle, and the anion the lowest energy transition. This is in fact observed. Therefore the present assignment of the features at 1820.4 and 549.5 cm^{-1} to the C–C stretching and H–C–C bending modes of the ethynyl cation is supported.

D. Matrix interactions

What can we make of the neon-to-argon solvent shifts for CCH, CCH$^-$ and CCH$^+$? With the gas phase C–C fundamental of CCH at 1840.6 cm^{-1} as a reference,[14] the argon matrix *blue* shifts CCH by 5.2 cm^{-1} and the neon matrix *red* shifts CCH by 4.1 cm^{-1} (just the opposite of most molecules) with a 9.3 cm^{-1} difference. The closed shell CCH$^-$ anion only differs by 2.3 cm^{-1} between neon and argon but the triplet CCH$^+$ cation has the largest 11.8 cm^{-1} difference, which is reasonable to expect. The matrix observations suggest that gaseous CCH$^+$ may absorb near 1840 cm^{-1} where the CCH radical will complicate observation of the cation.

What is the nature of CCH$^+$ isolated in solid argon and in solid neon? We believe that the present CCH$^+$ is a "free ion" trapped in these slightly polarizable solids. The small blue 11.8 cm^{-1} matrix shift in the HC–C$^+$ stretching fundamental from solid argon to solid neon suggests a relatively minor solvent effect. The best model is C$_2$H$_2^+$ for which the antisymmetric C–H stretching mode has been observed in the gas phase (3135.98 cm^{-1}),[62] solid neon (sites 3137.6,[28] and 3134 cm^{-1}) and solid argon (sites 3105.5,[28] and 3104.4 cm^{-1}). The neon matrix more nearly approximates the gaseous C$_2$H$_2^+$ cation, which argon slightly solvates and redshifts. Finally, note that the C–C stretching mode of C$_2$H$_2^+$ from the high-resolution photoelectron spectrum (1829.0 ± 2.5)[63] is between the present neon and argon matrix values for the C–C stretching mode of CCH$^+$.

E. Reaction mechanisms

In addition to energetic metal atoms, the laser ablation process produces metal cations and electrons,[64] and the latter may contribute to the spectrum if the separated charged species can be trapped. Recent studies in this laboratory have characterized O$_4^+$, O$_4^-$, (NO)$_2^+$, (NO)$_2^-$, and (CO)$_2^-$ in laser-ablation matrix isolation experiments.[44–48] The observation of C$_2$H$_2^+$ in these experiments clearly demonstrates that photons, electrons and/or metal atoms produced by ablation contain energy in excess of 11.40 eV, the ionization energy of acetylene,[63] and 11.6 eV, the ionization energy of CCH,[21,65]

$$C_2H_2 + \text{impact}(h\nu \text{ and/or } e) \rightarrow C_2H_2^+ + e^- \qquad (1a)$$

$$\rightarrow CCH + H. \qquad (1b)$$
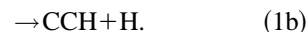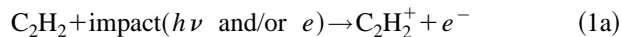
It is suggested that CCH$^+$ is made in the same manner as C$_2$H$_2^+$ by electron or photon impact during the condensation process,

$$CCH + \text{impact}(h\nu \text{ and/or } e) \rightarrow CCH^+ + e^-. \qquad (2)$$
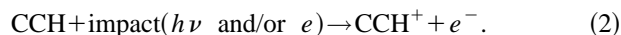
The formation of CCH$^-$ by electron capture is straightforward as the electron affinity of CCH is 2.97 eV,[26]

$$CCH + e^- \rightarrow CCH^-. \qquad (3)$$

The relative yield of CCH, CCH$^+$, and CCH$^-$ appears to vary with the metal target. Another variable is the radiation produced, which does photochemistry during the deposition process. Earlier laser-ablation experiments[66] with Mg and C$_2$H$_2$ produced the same CCH, CCH$^+$, and CCH$^-$ absorptions with an increased relative yield of CCH$^-$. In addition,

an argon discharge seeded with zinc, gave strong 2084.0, 2060.4, 1845.8, and 1770.5 cm^{-1} absorptions and a weak 1820.4 cm^{-1} band showing that the presence of extra electrons favors the 1770.5 cm^{-1} CCH$^-$ absorption.[66]

In the neon matrix experiments, with low laser power, doping with CO_2 adds additional electron traps, and CO_2^- is formed at the expense of CCH$^-$. The yield of CCH$^+$ is therefore favored over CCH. This evidence adds further support for the present identification of CCH$^+$ and CCH$^-$ in these experiments.

The matrix photochemistry merits comment. In the neon matrix, broadband photolysis decreases CCH$^-$ and increases the CCH radical, as observed by Jacox and co-workers,[28] and in these experiments photolysis decreases the CCH$^+$ absorption as expected due to neutralization by electrons detached from CCH$^-$. With CO_2 added as an electron trap, however, $\lambda > 290$ nm irradiation photoionizes CO_2^- and allows a slight increase in CCH$^-$ as the electron affinity of CCH is much higher than that for CO_2.[26,59] In the argon matrix experiments, in addition, the CCH$^+$ band increases 10% on broadband photolysis in uranium and some higher power titanium experiments while there is a 10% decrease in the CCH$^-$ band. We believe that the rigid 7 K argon matrix traps some U$^+$ and Ti$^+$ cations from laser ablation and these cations scavenge electrons from the photoionization of CCH$^-$ so that a small growth in the CCH$^+$ band can be observed. This may arise from a sequential two photon process using the intense mercury lines in the 270–280 nm region, precisely where REMPI transitions have been observed for gaseous CCH radical.[21] More likely, the growth in CCH$^+$ is from dissociation of $C_2H_2^+$, which is observed here, reaction (4). The appearance potential of CCH$^+$ is 5.4–5.8 eV above the ionization energy of C_2H_2, and this process is probably accompanied by considerable kinetic energy of decomposition.[67,68] Hence, the strong 5.0 eV mercury arc radiation is capable of dissociation reaction (4),

$$C_2H_2^+ + h\nu \rightarrow CCH^+ + H. \qquad (4)$$

VI. CONCLUSIONS

Laser-ablated transition, lanthanide, and actinide metals fragment acetylene to form several interesting transients. The trio of metal independent bands at 1845.8, 1820.4, and 1770.5 cm^{-1} in solid argon can be attributed to the primarily C–C stretching coordinates of the simple acetylene fragments CCH, CCH$^+$, and CCH$^-$, respectively. The CCH$^+$ cation is observed at 1832.2 cm^{-1} in corresponding neon experiments, and this band is *increased* while CCH$^-$ is *decreased* relative to the CCH radical upon the addition of CO_2 to serve as an electron trap. Unlike CCH and CCH$^-$ which have been observed previously, the present investigation provides the first infrared spectroscopic evidence for the CCH$^+$ cation. This CCH$^+$ is isolated in solid neon and solid argon. In addition to the absorption due to the C–C stretching mode of the ethynylium cation, a broad, intense feature at 549.5 cm^{-1} is assigned to a higher frequency component of the Renner–Teller split H–C–C bending mode of this species, further supporting the present identification of CCH$^+$. These three species have been modeled using quantum mechanical

calculations at the CCSD(T), BP86, and B3LYP levels of theory in order to provide additional support for the present assignments and to help understand these important transient species.

ACKNOWLEDGMENT

[1] A. Ohff, V. V. Burlakov, and U. Rosenthal, J. Mol. Catal. A **108**, 119 (1996).

[2] U. Pidun and G. Frenking, J. Organomet. Chem. **525**, 269 (1996).

[3] R. J. Strittmatter and B. E. Bursten, J. Am. Chem. Soc. **113**, 552 (1991).

[4] T. Straub, A. Haskel, and M. S. Eisen, J. Am. Chem. Soc. **117**, 6364 (1995).

[5] J. A. Warnatz, H. Bockhan, A. Moser, and H. W. Wenz, Int. Symp. Combust. Proc. **19**, 197 (1983).

[6] E. Bastin, J.-L. Delfau, M. Reuillon, C. Vovella, and J. Warnatz, Int. Symp. Combust. Proc. **22**, 313 (1988).

[7] W. W. Duley and D. A. Williams, *Interstellar Chemistry* (Academic, New York, 1984).

[8] E. I. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. **40**, 213 (1964).

[9] D. E. Milligan, M. E. Jacox, and L. Abouaf-Marquin, J. Chem. Phys. **46**, 4562 (1967).

[10] W. R. M. Graham, K. I. Dismuke, and W. Weltner, Jr., J. Chem. Phys. **60**, 3817 (1974).

[11] M. E. Jacox, Chem. Phys. **7**, 424 (1975).

[12] R. A. Shepherd and W. R. M. Grahan, J. Chem. Phys. **86**, 2600 (1987).

[13] M. E. Jacox and W. B. Olson, J. Chem. Phys. **86**, 3134 (1987).

[14] H. Kanamori, K. Seki, and E. Hirota, J. Chem. Phys. **87**, 73 (1987).

[15] H. Kanamori and E. Hirota, J. Chem. Phys. **88**, 6699 (1988).

[16] P. G. Carrick, A. J. Merer, and R. F. Curl, Jr., J. Chem. Phys. **78**, 3652 (1983).

[17] R. F. Curl, P. G. Carrick, and A. J. Merer, J. Chem. Phys. **82**, 3479 (1985); **83**, 4278 (1985).

[18] K. Kawaguchi, T. Amano, and E. Hirota, J. Mol. Spectrosc. **131**, 58 (1988).

[19] J. W. Stephens, W.-B. Yan, M. L. Richnow, H. Solka, and R. F. Curl, J. Mol. Struct. **190**, 41 (1988).

[20] J. M. Brown and K. M. Evenson, J. Mol. Spectrosc. **131**, 161 (1988).

[21] T. A. Cool and P. M. Goodwin, J. Chem. Phys. **94**, 6978 (1991).

[22] M. E. Jacox, J. Phys. Chem. Ref. Data **3**, 32 (1994), and references therein.

[23] D. Forney, M. E. Jacox, and W. E. Thompson, J. Mol. Spectrosc. **170**, 178 (1995).

[24] B. M. Hughes, C. Lifslitz, and T. O. Tierman, J. Chem. Phys. **59**, 3162 (1973).

[25] B. K. Janousek, J. I. Brauman, and J. Simons, J. Chem. Phys. **71**, 2057 (1979).

[26] K. M. Ervin and W. C. Lineberger, J. Chem. Phys. **95**, 1167 (1991).

[27] T. R. Taylor, C. Xu, and D. M. Neumark, J. Chem. Phys. **108**, 10018 (1998).

[28] D. Forney, M. E. Jacox, and W. E. Thompson, J. Mol. Spectrosc. **153**, 680 (1992).

[29] D. K. Bohme, S. Wlodek, L. Williams, L. Forte, and A. Fox, J. Chem. Phys. **87**, 6934 (1987).

[30] W. De Lange and N. M. M. Nibbering, Int. J. Mass Spectrom. Ion Processes **86**, 287 (1988).

[31] G. B. Scott, D. A. Fairley, C. G. Freeman, M. J. McEwan, N. G. Adams, and L. M. Babcock, J. Phys. Chem. A **101**, 4973 (1997).

[32] J. A. Montgomery and C. E. Dykstra, J. Chem. Phys. **71**, 1380 (1979).

[33] R. Krishnan, M. J. Frisch, R. A. Whiteside, J. A. Pople, and P. von R. Schleyer, J. Chem. Phys. **74**, 4213 (1981).

[34] R. Glaser, J. Am. Chem. Soc. **109**, 4237 (1987).

[35] A. Largo and C. Barrientos, Chem. Phys. **138**, 291 (1989).

[36] L. A. Curtiss and J. A. Pople, J. Chem. Phys. **91**, 2420 (1989).

[37] S. Hashimoto, S. Iwata, and Y. Osamura, Chem. Phys. Lett. **174**, 649 (1990).

[38] W. Koch and G. Frenking, J. Chem. Phys. **93**, 8021 (1990).

[39] A. O'Keefe, R. Deraiard, and M. T. Bowers, J. Chem. Phys. **91**, 161 (1984).

[40] D. Zajfman, Z. Vager, R. Naaman, R. E. Mitchell, E. P. Kanter, T. Graber, and A. Belkacem, J. Chem. Phys. **94**, 6377 (1991).

[41] T. R. Burkholder and L. Andrews, J. Chem. Phys. **95**, 8697 (1991).

[42] L. Andrews, T. R. Burkholder, and J. T. Yustein, J. Phys. Chem. **96**, 10182 (1992).

[43] G. V. Chertihin and L. Andrews, J. Phys. Chem. **99**, 6356 (1995).

[44] G. V. Chertihin and L. Andrews, J. Chem. Phys. **105**, 2561 (1996).

[45] G. V. Chertihin, W. Saffel, J. T. Yustein, L. Andrews, M. Neurock, A. Ricca, and C. W. Bauschlicher, Jr., J. Phys. Chem. **100**, 5261 (1996).

[46] G. V. Chertihin and L. Andrews, J. Chem. Phys. **108**, 6404 (1998).

[47] L. Andrews, M. F. Zhou, S. P. Willson, G. P. Kushto, A. Snis, and I. Panas, J. Chem. Phys. **109**, 177 (1998).

[48] M. F. Zhou, G. V. Chertihin, and L. Andrews, J. Chem. Phys. **109**, 10893 (1998).

[49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, GAUSSIAN 94, Gaussian Inc., Pittsburgh, Pennsylvania, 1995.

[50] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[51] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[52] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[53] C. Lee, W. Yang, and R. Parr, Phys. Rev. B **37**, 785 (1988).

[54] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1385 (1993).

[55] K. I. Dismuke, W. Graham, and W. Weltner, Jr., J. Mol. Spectrosc. **57**, 127 (1975).

[56] L. N. Shen, T. J. Doyle, and W. Graham, J. Chem. Phys. **93**, 1597 (1990).

[57] K. O. Patten and L. Andrews, J. Phys. Chem. **90**, 3910 (1986).

[58] J. T. Godbout, T. M. Halasinski, G. E. Leroi, and J. Allison, J. Phys. Chem. **100**, 2892 (1996).

[59] M. E. Jacox and W. E. Thompson, J. Chem. Phys. **91**, 1410 (1989).

[60] H. Kanamori and E. Hirota, J. Chem. Phys. **89**, 3962 (1988).

[61] G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).

[62] M. W. Crofton, M.-F. Jagood, B. D. Rehfuss, and T. Oka, J. Chem. Phys. **86**, 3755 (1987).

[63] J. E. Reutt, L. S. Wang, J. E. Pollard, D. J. Trevor, Y. T. Lee, and D. A. Shirley, J. Chem. Phys. **84**, 3022 (1986).

[64] H. Kang and J. L. Beauchamp, J. Phys. Chem. **89**, 3364 (1985).

[65] A. G. Koures and L. B. Harding, J. Phys. Chem. **95**, 1035 (1991).

[66] C. A. Thompson and L. Andrews, J. Am. Chem. Soc. **118**, 10242 (1996); G. P. Kushto and L. Andrews (unpublished).

[67] R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, J. Chem. Phys. **44**, 1271 (1966).

[68] Y. Ono and C. Y. Ng, J. Chem. Phys. **74**, 6985 (1981).