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Vibrational and Electronic Spectra of Neutral and Ionic Combustion Reaction Intermediates Trapped in Rare-Gas Matrixes

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ABSTRACT
The infrared absorptions of neutral and ionic molecules trapped in solid rare-gas matrixes lie close to the gas-phase band centers, and perturbations in valence electronic transitions are relatively small. Since molecular diffusion through rare-gas solids is inhibited, matrix isolation studies provide a valuable tool for obtaining the infrared and visible−ultraviolet spectra of combustion reaction intermediates. The results of studies of the spectra of HCO, *trans*-HOCO, HCC, C_2^-, CO_2^+, CO_2^-, $C_2H_2^+$, $C_3H_4^+$, $HCOOH^+$, $HOCO^+$, and HCO_2^- summarized in this Account illustrate the importance of supplementing familiar generalizations with experimental observations.

Introduction

Fifty years ago, many chemical reactions had been shown to involve free radical intermediates. However, because of their great chemical reactivity, very few of these intermediates had been detected. In 1954, Whittle, Dows, and Pimentel[1] suggested that it might be possible to build up observable concentrations of free radicals and other highly reactive species by trapping them in dilute solid solution in an inert, rigid, optically transparent material, the matrix. Suitable sources of reactive species included sampling of pyrolysis, discharge, and chemical reaction systems, as well as photolysis of an appropriate precursor.

More than 5000 papers applying the matrix isolation technique have since been published. The earliest ones successfully tested the isolation properties of such matrix materials as argon and nitrogen at 14 K. Although a number of in situ photolysis studies of free radical precursors such as diazomethane initially gave disappointing or puzzling results, in 1960 Ewing and co-workers[2] identified infrared absorptions of HCO, formed by the reaction of photolytically generated H atoms with a CO matrix. One of the early members of the Pimentel group, Dolphus E. Milligan, believed that cage recombination presented a significant complication for in situ photolysis studies in matrixes but that if atoms were somewhat mobile in matrixes atom−molecule reactions might yield free radicals in that environment. He successfully tested this hypothesis by isolating small concentrations of HI and O_2 in an argon matrix and demonstrating the production of HO_2 on subsequent mercury-arc irradiation. All three of the vibrational fundamentals of HO_2, an important combustion reaction intermediate, were identified for the first time.[3]

Although spectroscopic data are now available for many free radicals both in the gas phase and trapped in a matrix environment, matrix isolation studies still offer important advantages. They permit spectral observations from the far-infrared well into the vacuum ultraviolet. All products are detectable if a suitably broad spectral region is studied. Reactions can be stopped at their initial stages, and energy-rich intermediates can be stabilized. Subsequent photodecomposition of the initially trapped intermediate can also be studied.

General aspects of matrix isolation spectroscopy have recently been surveyed.[4] This Account will review its application to obtaining spectra of combustion reaction intermediates.

Spectrum of HCO

Both the CO- and the CH-stretching frequencies of HCO behave anomalously. Although typically the CO-stretching fundamental for a carbonyl bond appears between 1700 and 1775 cm^{-1},[5] Ewing and co-workers[2] identified that fundamental of HCO at 1861 cm^{-1}. Milligan and Jacox[6] confirmed that result and identified the CH-stretching fundamental at 2488 cm^{-1}, compared to typical values[5] between 2750 and 3000 cm^{-1}. Both laboratories identified the bending fundamental of HCO at 1090 cm^{-1}. Later, Milligan and Jacox[7] observed the three vibrational fundamentals of HCO trapped in an argon matrix at 2483, 1863, and 1087 cm^{-1}, close to the CO-matrix values. Later studies by many workers support these observations.[8] Although the gas-phase band centers for the two lower frequency fundamentals, 1868.17 and 1080.76 cm^{-1}, lie close to the matrix isolation values, that for the CH-stretching vibration, 2434.48 cm^{-1}, is even lower than the matrix value.

The anomalous positions of the CO- and CH-stretching fundamentals of HCO suggest that predictions of vibrational frequencies of free radicals using characteristic group frequency generalizations from molecules that have no unpaired electrons sometimes are severely mistaken.

For many years, a complicated emission band system between about 235 and 475 nm that appeared on combustion of a variety of hydrocarbons, the “hydrocarbon flame bands”, was believed to be contributed by HCO but could not be definitively assigned. High-resolution analysis of some of the bands by Dixon[9] indicated that the lower

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state of the emission was the ground state of HCO and provided other information valuable in the final assignment. The absorption bands corresponding to this emission band system, between 210 and 260 nm, were observed by Milligan and Jacox[7] for HCO trapped in argon and CO matrixes. Given the ground-state fundamental frequencies and the positions of the ultraviolet absorptions, it became possible to assign most of the emission bands. Later sophisticated laser-based studies by Sappey and Crosley,[10] Adamson and co-workers,[11] and others have yielded much information on this band system.[8] The results are generally consistent with the matrix observations.

Reaction of OH with CO

As the major mode for the production of CO_2 from CO in combustion systems, the reaction of OH with CO has received much study. Ab initio calculations by Kudla and co-workers[12] indicate that the most strongly bound intermediate is *trans*-HOCO, which has a significant barrier to isomerization to *cis*-HOCO, slightly higher in energy. HCO_2 is higher yet in energy, with substantial barriers to rearrangement. Direct reaction of H with CO_2 to form either HCO_2 or *cis*-HOCO also has a significant barrier; neither process can occur at cryogenic temperatures.

Spectroscopic studies of matrix-isolated *trans*-HOCO have yielded five of its six vibrational fundamentals. The 122-nm photolysis of H_2O in a CO matrix produced both *cis*- and *trans*-HOCO.[13] A later argon-matrix study[14] using formic acid as the precursor gave only *trans*-HOCO. The frequency of its carbonyl stretching fundamental was exceptionally high. Hydrogen bonding of *trans*-HOCO to the CO matrix lowers its OH-stretching fundamental by 150 cm^{-1} and raises its HOC-bending fundamental by 50 cm^{-1} compared to the argon-matrix positions. The band centers for both the OH-stretching fundamental[15] and the CO-stretching fundamental[16] of *trans*-HOCO obtained in later high-resolution gas-phase studies agree within 1% with the argon-matrix values.

Gas-Phase versus Matrix Observations

Infrared absorptions of many molecules have now been identified both in the gas phase and in rare-gas matrixes. By January 2001, 426 ground-state fundamentals of small reaction intermediates had been identified both in the gas phase and in argon matrixes and 168 both in the gas phase and in neon matrixes. Comparison[4] gave a numerical average (gas−matrix) deviation of −0.03% for a neon matrix and of 0.21% for an argon matrix. Although the argon-matrix distribution is somewhat broader than that for the neon matrix, for both matrixes most of the fundamental absorptions lie within 1% of the gas-phase band centers, and very few deviate by more than 2%.

Several reviews provide detailed vibrational and electronic spectral data for reaction intermediates in both the gas phase and inert matrixes.[8,17,18] In addition, a computer-searchable database is included in the NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>).

Because electron correlation is very important for species with one or more unpaired electrons, obtaining physically realistic results for them from ab initio and density functional calculations presents an exceptionally great challenge. Byrd and co-workers[19] tested frequently used "package" calculations of ground-state structures and vibrational fundamentals of free radicals. They concluded that Hartree−Fock calculations have unacceptably large deviations and that MP2 calculations are erratic. CCSD, CCSD(T), and B3LYP calculations have the smallest vibrational frequency deviations, but even for the most sophisticated basis sets surveyed (cc-pVDZ and cc-pVTZ), the average deviations were several times as large as those for neon- or argon-matrix observations. More sophisticated calculations can give closer agreement with experiment, but there remains much room for both further experimental studies and refinement of calculational procedures. Dialogue between experimentalists and theoreticians promises to be mutually beneficial.

Vacuum-Ultraviolet Photolysis of C_2H_2 in Rare-Gas Matrixes

Early workers ascribed a 520-nm band system to the Swan bands of triplet C_2 isolated in inert matrixes. Although the location of the band system was appropriate, the upper- and lower-state band separations in argon-matrix observations were 1955 and 1771 cm^{-1}, respectively, compared to gas-phase values of 1755 and 1618 cm^{-1} for the Swan bands. In the early days of matrix isolation, this disparity was ascribed to "matrix effects".

In 1963, Ballik and Ramsay[20] reported that the true ground state of C_2 is X $^1\Sigma_g^+$, 610(5) cm^{-1} below the lower state of the Swan bands. This implied that excited-state C_2 was stabilized in matrixes. Milligan and co-workers[21] studied the 122-nm photolysis of isotopically enriched C_2H_2 trapped in rare-gas solids. The Mulliken band and the Phillips bands of singlet C_2 were prominent, demonstrating that deactivation to the ground state was a major process. However, the "Swan bands" also were prominent and were very sharp. These bands were unshifted for C_2D_2, and studies on ^{13}C-enriched acetylene gave splittings appropriate for C_2. For the time being, the puzzle remained unresolved.

Vibronic Spectrum of HCC

In the same experiments, an absorption at 1846 cm^{-1} was assigned to HCC, a species important in such diverse fields as combustion and astrophysics. Thus began a complex chain of discoveries. Later argon-matrix experiments[22] showed that a prominent absorption near 3600 cm^{-1} was also contributed by HCC, and subsequent gas-phase observations in several laboratories led to the identification of many other infrared bands associated with HCC and DCC. Shepherd and Graham[23] observed the argon-matrix counterparts of these gas-phase absorptions and found additional bands of HCC up to 4600 cm^{-1}. Their assignment of an absorption at 2104 cm^{-1} to the $(\nu_2 + \nu_3)$ combination band suggested that ν_2 lies near 260 cm^{-1},

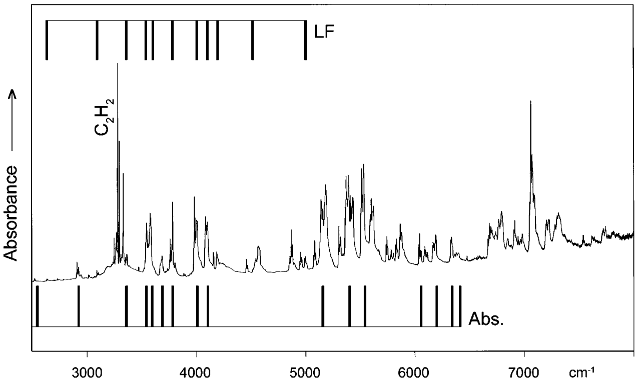

FIGURE 1. Near-infrared absorption of HCC isolated in solid neon. LF denotes gas-phase laser-excited fluorescence (see ref 29); Abs denotes gas-phase absorption band centers.

an anomalously low value. Jacox and Olson[24] surveyed the infrared and near-infrared absorption spectra of HCC and DCC trapped in solid argon and found approximately 50 absorptions of HCC between 4200 and 7900 cm^{-1}, a phenomenon attributable to strong vibronic interaction between the ground state (which, because of the very low-frequency bending fundamental, has many near-infrared levels of Π symmetry) and the low-lying $\tilde{A}\ ^2\Pi$ state.

Subsequent experiments confirmed and extended these assignments. Diode laser studies[25,26] demonstrated that the gas-phase band center for ν_2 of HCC lies at 371.60 cm^{-1}. The lower value inferred from the combination band results from strong vibronic interaction between ground-state ($\nu_2 + \nu_3$) and the low-lying $\tilde{A}\ ^2\Pi$ state. Neon-matrix observations of normal and isotopically substituted HCC, illustrated in Figure 1, were subsequently extended to 12 000 cm^{-1}.[27] Both the assignments suggested by ab initio calculations[28] and the observed carbon-13 shifts were considered, yielding revised assignments for many of the prominent bands. Hsu[29] reported an analysis of the fluorescence bands, which arise from laser excitation of HCC to its $\tilde{B}$ state, near 39 000 cm^{-1}, and terminate in levels below about 5000 cm^{-1}. Taking into account that some of the levels are strongly mixed, her assignments are consistent with those proposed in the neon-matrix study. The positions of the levels derived from the fluorescence experiments, designated by "LF", are shown in Figure 1.

Significant studies on this important problem are in progress. An ongoing gas-phase near-infrared diode laser absorption by Tokaryk[30] has permitted assignment of five bands of HCC, four of which arise from the ground state, between 6000 and 6500 cm^{-1}. The positions of the gas-phase absorption band centers between 2500 and 6500 cm^{-1} are also shown in Figure 1. The agreement between the neon-matrix and gas-phase observations is good. Refinement of the ab initio calculations is also in progress.[31] These new calculations, which include carbon-13 isotopic shifts, should facilitate definitive assignments for the higher frequency bands of HCC.

Spectrum of C_2^-

In 1968, Herzberg and Lagerqvist[32] identified a new C_2 band system with origin near that of the Swan bands. All of the low-lying electronic transitions of C_2 that were predicted by molecular orbital theory had already been assigned. They noted that the behavior of this band system was appropriate for C_2^-, demonstrated to be present in their system, but a definitive assignment was not possible. Confirmation of the identification of C_2^- would provide the first spectrum of a gas-phase anion.

In several conversations and in a letter to D. E. Milligan dated 5 December 1968, Prof. Herzberg noted the similarity between the "Swan bands" of the matrix experiments and his new C_2 band system and urged further experiments. In part, his letter reads as follows (reproduced with permission):

> "...on re-reading your paper it still appears to me that there is a case to be made for the assumption that the band system near 5200 Å that you find in the matrix is identical with the new spectrum that we have observed in the paper just published. The shift in the argon matrix is, of course, fairly large but is much smaller in the neon matrix, but the most important argument for such an identification is the much better agreement of the vibrational intervals in the upper and lower state as compared with the identification of your bands as Swan bands.
>
> "While I feel rather strongly that the evidence for C_2^- is fairly strong we could not eliminate the possibility of fairly highly excited states of neutral C_2, but this would be eliminated if the bands are observed in the matrix at low temperature.
>
> "The other point that intrigues me is your observation that the spectrum disappears on irradiation with light below 2800 Å. This would be exactly what one might expect for C_2^- since the electron affinity is estimated to be between 3 and 4 eV, but is difficult to understand on the assumption that your bands are the Swan bands since the dissociation energy of C_2 is now generally agreed to be 6.2 eV."

Encouraged by this communication, Milligan and Jacox[33] conducted new experiments in which a supplementary source of photoelectrons, usually cesium atoms, was added to the sample. As is shown in Figure 2, the results were dramatic. The intensity of the Mulliken band of singlet C_2 was sufficiently decreased and that of the 5200 Å (520 nm) band system sufficiently enhanced to reverse their relative intensities. The 520-nm band system was no longer destroyed by 280-nm radiation, since photodetachment from cesium occurs under those conditions and the resulting electrons can reattach to C_2. These results strongly supported the C_2^- assignment. A definitive iden-

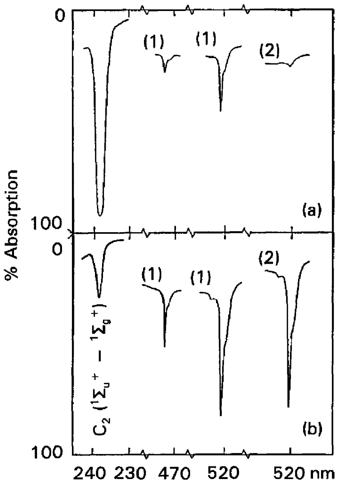

FIGURE 2. (a) $Ar/C_2H_2 = 1000$, deposited with concurrent 122-nm irradiation; (b) $Ar/C_2H_2 = 1000 + Cs$, deposited, then exposed to 122-nm radiation; (2) subsequent Hg-arc irradiation.

tification of C_2^- later resulted from the two-photon photodetachment study by Lineberger and Patterson.[34]

The matrix study yielded several other important conclusions. No evidence remained for the trapping of excited-state molecules in rare-gas matrixes. Anions can be stabilized in rare-gas matrixes, implying that cations are also stabilized. Photoionization of an alkali metal provides a suitable electron source for anion stabilization. Subsequently, the electronic spectrum of C_2^+ was detected first in a neon matrix[35] and then in the gas phase[36] in the laboratory of Maier. The spectroscopy of larger C_n species and of their ions has been surveyed by Weltner and Van Zee,[37] and much more recent spectroscopic data for those species can be found in the vibrational and electronic energy level reviews.[8,17,18]

Stabilization of Molecular Ions

Because small molecular ions have a probability of reacting on a single collision that often exceeds 10%, obtaining their optical spectra has been difficult. The challenge is important, since optical spectroscopy can provide much new information about ions. Unlike mass spectroscopy, optical spectroscopy is amenable to remote sensing. Infrared spectra yield ground-state vibrational frequencies, which in turn give information regarding ground-state molecular structures—of special interest since often isomerization accompanies ion formation. The high reaction probability of ions also makes feasible stabilization and study in matrixes of binary ion—molecule complexes.

Since the identification of C_2^-, spectra have been reported for many other ionic species trapped in rare-gas matrixes. The subject has recently been surveyed.[4] Here, attention will be focused on neon-matrix studies in this laboratory of ions of interest to the combustion scientist, including a number of cations (CO_2^+, $C_2H_2^+$, $C_3H_4^+$, and $HOCO^+$) and anions (C_2^-, HCO_2^-) found by Hayhurst and Kittelson[38] to be present in appreciable concentration in oxy-acetylene flames.

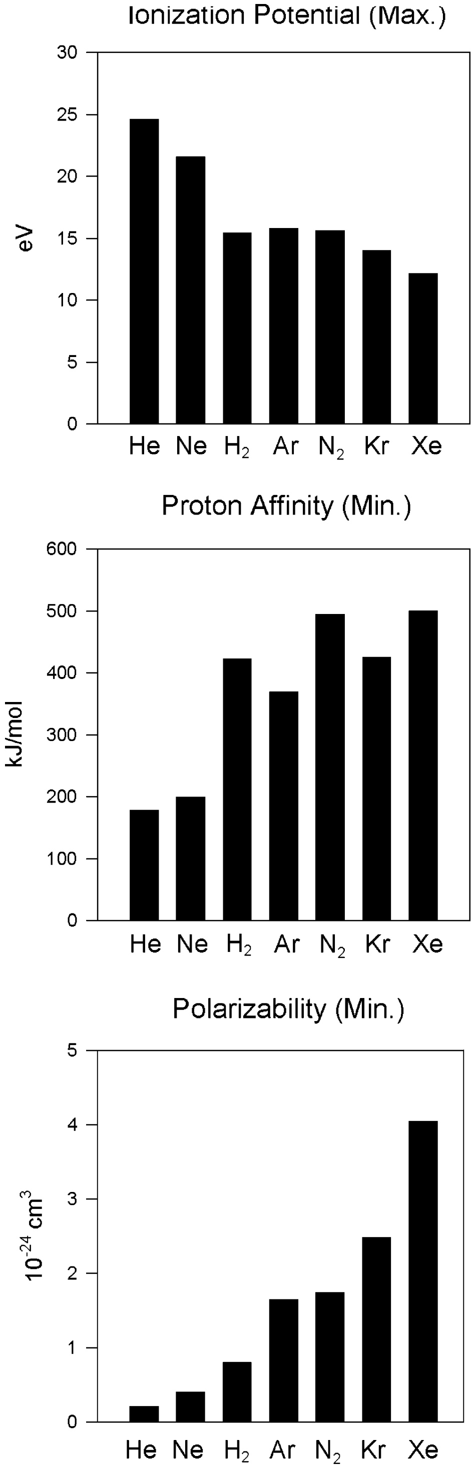

FIGURE 3. Matrix properties needed to minimize ion—matrix interactions (optimum magnitude in parentheses).

Of all the solid matrix materials, neon is best suited for ion studies. As is shown in Figure 3, not only its high ionization potential but also its relatively low proton affinity and polarizability favor minimal perturbation of ions by the neon matrix. Only helium surpasses neon in those criteria. Studies of ions in helium clusters provide a future challenge. Not only protons but also other ionic species can sometimes react even with neon—a comparatively rare but chemically interesting phenomenon.

The experimental configuration used for the stabilization of ions in neon matrixes was described in the first paper of the series.[39] Very pure neon streams through a quartz tube, where it is excited by a microwave power source, and expands into the cryogenic cell through a coarse pinhole. Neon resonance radiation and metastable neon atoms can interact with the molecule XY, which is introduced beyond the discharge region. The resulting mixture is frozen onto the observation surface, maintained at 4.2 K. Product identifications for many systems have shown that fragmentation of XY in the discharge region is minimal and that the observable products are governed by the lowest excited energy levels of neon, between 16.6 and 16.84 eV, sufficient to ionize all atoms and molecules except neon and helium.

Ions Produced from CO_2. CO_2 was used to test this configuration.[39] The first ionization energy of CO_2 is 13.8 eV, and the gas-phase band center for ν_3 of CO_2^+ had previously been identified[40] at 1423.08 cm^{-1}. The ν_3 absorption of CO_2^+ trapped in solid neon appeared at 1421.7 cm^{-1}, only 1.4 cm^{-1} below the gas-phase band center. The ν_3 fundamental of CO_2^-, produced as a result of photoelectron capture by CO_2, appeared at 1658.3 cm^{-1}. A later study[41] identified the remaining infrared-active fundamentals of CO_2^+ and CO_2^- isolated in a neon matrix.

Often it has been convenient to assume that the structures and vibrational fundamental frequencies of small neutral molecules are similar to those of the corresponding cation or anion. The CO_2 ion studies illustrate the failure of this assumption. Unlike CO_2 and CO_2^+, which are linear, CO_2^- is bent, with a calculated valence angle of 137°. The antisymmetric stretching fundamental, ν_3, of CO_2 lies at 2349.16 cm^{-1}, compared to 1423.08 and near 1658.3 cm^{-1} for CO_2^+ and CO_2^-, respectively.

Ionization of C_2H_2. The gas-phase band center for $C_2H_2^+$ has been identified at 3135.98 cm^{-1}.[42] The corresponding neon-matrix absorption appeared at 3137.6 cm^{-1} in a study of C_2H_2 using this configuration.[43]

Infrared Spectrum of $C_3H_4^+$. Near 16.6 eV, the major cation produced from gas-phase allene or propyne is *cyc*-$C_3H_3^+$, which, as the simplest aromatic cation, is exceptionally stable.

Several new infrared absorptions appeared when a Ne/allene mixture was subjected to excited neon atoms and their resonance radiation.[44] Changes in the spectrum on exposure of the deposit to selected wavelength ranges of visible and ultraviolet radiation were also studied, a procedure that is very useful for sorting the products in such experiments. Six absorptions, designated as type A, behaved similarly under those conditions. Their positions are shown in Figure 4. Four of these absorptions corresponded well with the infrared-active fundamentals of *cyc*-$C_3H_3^+$ in its polycrystalline salts.[45] They also agreed well with the results of density functional calculations, considering the substantial anharmonic shift in the high-frequency degenerate CH-stretching fundamental. The two extra absorptions in the CH-stretching region could arise from combination bands or from another species with similar behavior on filtered irradiation.

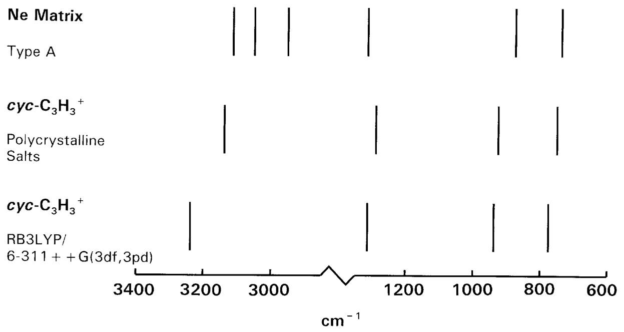

FIGURE 4. Infrared-active fundamentals of *cyc*-$C_3H_3^+$ compared with absorptions observed in a neon matrix (values for polycrystalline salts from ref 45).

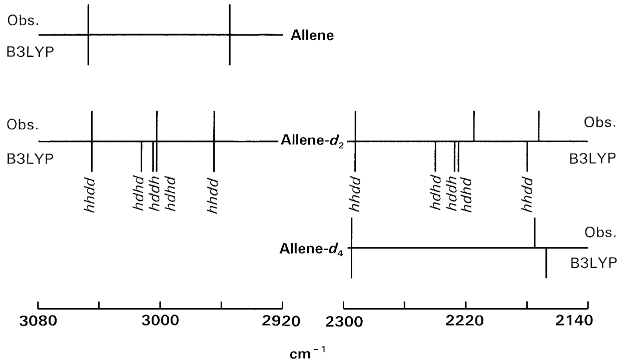

FIGURE 5. CH- and CD-stretching absorptions of allene-d_n cation (6-311++G(3df,3pd) basis set; CH- and CD-stretching frequencies scaled by 0.965 and 0.977, respectively).

Agreement of observed and calculated vibrational frequencies is not a *sufficient* condition for free radical or molecular ion identification. Comparison of observed and calculated isotopic shifts provides additional support, as well as information on molecular structures and chemical bonding properties. The match of the isotopic substitution frequency pattern near 1300 cm^{-1} to that for *cyc*-$C_3H_3^+$ is unsatisfactory, but that to the allene cation, the other likely product, is good. In Figure 5, the positions of the observed CH- and CD-stretching fundamentals are compared with those calculated for the allene-d_n cation using the UB3LYP/6-311++G(3df,3pd) procedure. (The weak absorption at 3105.7 cm^{-1} may reasonably be attributed to a combination band.) The calculated CH- and CD-stretching frequencies were scaled by factors of 0.965 and 0.977, respectively, to match the highest calculated frequency to the highest observed frequency. In the allene-d_2 experiments, the starting material was $H_2C{=}C{=}CD_2$, the isotopomer designated as 'hhdd'. Because the angle between the planes of the two CH_2 groups of the cation is approximately 50°, two additional isomers of formula $HDC{=}C{=}CHD$ can appear if the ionization process involves H-atom migration. The agreement is reasonable, and the results suggest that H-atom migration does occur.

The same type A absorptions predominated in experiments starting with CH_3CCH, again suggesting that H-atom migration occurs. A detailed mechanism for this migration was proposed by Frenking and Schwarz.[46] In

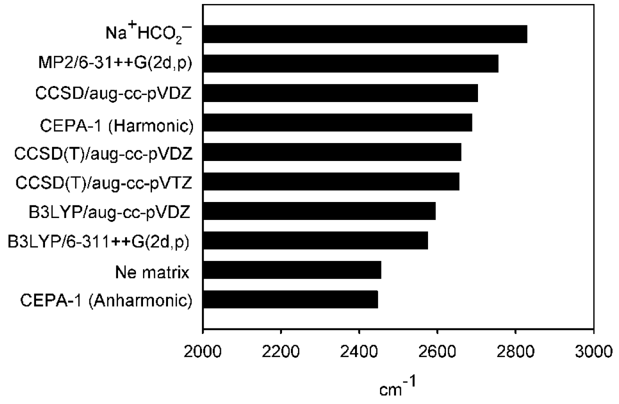

FIGURE 6. Position of CH-stretching fundamental of HCO_2^-.

the gas phase, the lifetime of the $C_3H_4^+$ cation is long enough for the propyne cation to isomerize to the more stable allene cation before H-atom detachment occurs. In the neon matrix, rapid collisional deactivation of the allene cation suppresses H-atom detachment.

Ions Derived from Formic Acid. Several products occur when formic acid is co-deposited in a neon matrix with excited neon atoms and their resonance radiation.[47] In the gas phase, the threshold for $HCOOH^+$ production from HCOOH is 11.33 eV,[48] the onset of $HOCO^+$ production occurs near 12.4 eV,[49,50] and at higher energies $HOCO^+$ predominates. These two cations are also expected to be formed in the Ne/HCOOH experiments. The same products appear in experiments using a Ne/H_2/CO_2 mixture[51] instead of Ne/HCOOH, greatly facilitating the use of isotopic substitution for product identification. The first ionization energy of CO_2 is 13.8 eV, and that of H_2 is 15.4 eV. No fragment ions appear from either species below 16.84 eV, the energy limit for this sampling configuration.

Five prominent infrared absorptions in both systems are readily assigned to *trans*-HOCO. The OH- and CO-stretching absorptions of this species approach the gas-phase values even more closely than do their argon-matrix counterparts.

Three of the four prominent absorptions that grew on filtered visible and mercury-arc irradiation of the deposit but were readily destroyed by 254-nm mercury-arc radiation lie close to infrared absorptions of polycrystalline $Na^+HCO_2^-$.[52] The fourth absorption, at 2456 cm^{-1}, has a carbon-13 isotopic shift appropriate for an exceptionally low-frequency CH-stretching fundamental. A wide variety of ab initio and density functional calculations, summarized in Figure 6, give harmonic frequencies for the CH-stretching fundamental of HCO_2^- that are smaller than the previously assigned frequency. Correction for anharmonicity would further decrease the calculated frequencies. The anharmonic CEPA-1 calculation by Botschwina[53] yielded a frequency of 2447 cm^{-1}, 9 cm^{-1} below the neon-matrix value. Recently, Pelc and co-workers[54] reported a maximum at 1.25 eV for the production of HCO_2^- upon dissociative attachment of low-energy electrons to gas-phase HCOOH. It is concluded that HCO_2^-, an important combustion reaction intermediate, is stabilized in the neon matrix after formation by dissociative electron attachment to HCOOH and that it has its CH-stretching fundamental near 2456 cm^{-1}, implying an exceptionally weak CH bond.

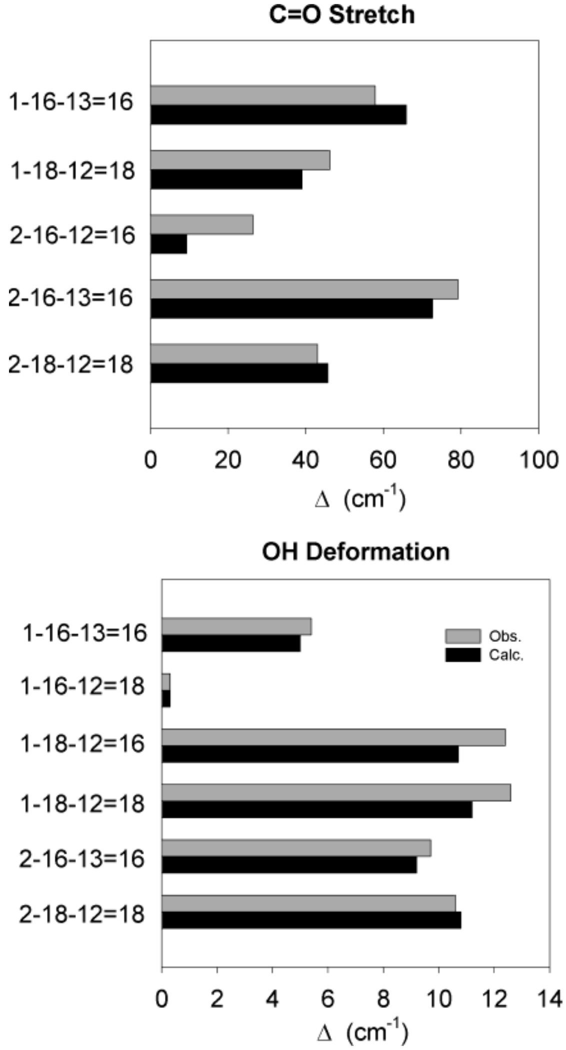

FIGURE 7. Isotopic shifts for $HOCO^+$. Isotopic species are designated by their atomic masses (e.g., $H^{16}O^{13}C^{16}O^+$ by 1−16−13=16).

Recent photoelectron spectroscopic studies[49,50] of HCOOH yielded four vibrational fundamentals of ground-state $HCOOH^+$ with 20 cm^{-1} uncertainties. One of these fundamentals, at 1495(20) cm^{-1}, is close to the 1497.7 cm^{-1} neon-matrix absorption. Relatively few molecules containing only C, H, and O have vibrational fundamentals near 1500 cm^{-1}. That absorption and three others were destroyed when the deposit was subjected to prolonged irradiation at wavelengths longer than 695 nm, consistent with the known predissociation of $HCOOH^+$ in its low-lying first excited electronic state. Their isotopic shifts correspond well with those predicted by density functional calculations for $HCOOH^+$. Taken together, the photoelectron and neon-matrix results identify the positions of seven of the nine vibrational fundamentals of $HCOOH^+$.

Only the OH-stretching fundamental of $HOCO^+$ has previously been identified; Amano and Tanaka[55,56] determined its gas-phase band center at 3375.37 cm^{-1}. This fundamental absorption is lowered by 120 cm^{-1} when $HOCO^+$ is complexed with a single neon atom.[57] When proton capture by the rare gas competes with that by a small molecule, as for $Ar_n\cdots HCO^+$,[58] the shift in the H-stretching frequency is greatest for $n = 1$ and somewhat smaller for larger values of n. Thus, the OH-stretching fundamental of $HOCO^+$ trapped in a neon matrix should appear between 3375 and 3255 cm^{-1}.

Undulations in the HOCO photoionization yield curve near its threshold[59] suggest that another vibrational fundamental of $HOCO^+$ should lie near 2300 cm^{-1}.

In neon-matrix experiments, absorptions at 3280, 2400, and 1020 cm^{-1} are little changed on prolonged irradiation of the deposit at wavelengths longer than 695 nm but disappear readily when the cutoff wavelength is 420 nm. The 3280 cm^{-1} absorption has isotopic substitution behavior appropriate for an OH-stretching vibration and is in the expected region for that fundamental of $HOCO^+$. As is shown in Figure 7, the isotopic shift patterns for the 2400 and 1020 cm^{-1} absorptions are appropriate for their assignment to the C═O stretching and OH-deformation fundamentals, respectively, of $HOCO^+$.

Conclusions

The ground-state structures, chemical bonding properties, and vibrational energy levels of small polyatomic free radicals and molecular ions may differ considerably from those of related stable molecules or from results of ab initio calculations that do not adequately treat electron correlation. Spectroscopic observations on samples in which the species of interest is trapped in a large excess of solid neon or argon have yielded new information regarding the vibrational and electronic energy levels of a variety of neutral and ionic combustion reaction intermediates. This information should facilitate the development of probes for these intermediates and of more sophisticated computational procedures for molecules that have a high degree of electron correlation.

It's still worth doing experiments!

References

(1) Whittle, E.; Dows, D. A.; Pimentel, G. C. Matrix Isolation Method for the Experimental Study of Unstable Species. *J. Chem. Phys.* **1954**, *22*, 1943.
(2) Ewing, G. E.; Thompson, W. E.; Pimentel, G. C. Infrared Detection of the Formyl Radical HCO. *J. Chem. Phys.* **1960**, *32*, 927−932.
(3) Milligan, D. E.; Jacox, M. E. Infrared Spectroscopic Evidence for the Species HO_2. *J. Chem. Phys.* **1963**, *38*, 2627−2631.
(4) Jacox, M. E. The Spectroscopy of Molecular Reaction Intermediates Trapped in the Solid Rare Gases. *Chem. Soc. Rev.* **2002**, *31*, 108−115.
(5) Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*; Wiley: New York, 1957.
(6) Milligan, D. E.; Jacox, M. E. Infrared Spectrum of HCO. *J. Chem. Phys.* **1964**, *41*, 3032−3036.
(7) Milligan, D. E.; Jacox, M. E. Matrix-Isolation Study of the Infrared and Ultraviolet Spectra of the Free Radical HCO. The Hydrocarbon Flame Bands. *J. Chem. Phys.* **1969**, *51*, 277−288.
(8) Jacox, M. E. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules. Supplement B. *J. Phys. Chem. Ref. Data* **2003**, *32*, 1−441.
(9) Dixon, R. N. Rotational Structure of Some Hydrocarbon Flame Bands. *Trans. Faraday Soc.* **1969**, *65*, 3141−3149.
(10) Sappey, A. D.; Crosley, D. R. Laser-Induced Fluorescence in the $\tilde{B}$-$\tilde{X}$ System of the HCO Radical. *J. Chem. Phys.* **1990**, *93*, 7601−7608.
(11) Adamson, G. W.; Zhao, X.; Field, R. W. The HCO $\tilde{B}\ ^2A'\leftrightarrow\tilde{X}\ ^2A'$ System: Fluorescence Excitation and Stimulated Emission Pumping Spectra. *J. Mol. Spectrosc.* **1993**, *160*, 11−38.
(12) Kudla, K.; Schatz, G. C.; Wagner, A. F. A Quasiclassical Trajectory Study of the OH + CO Reaction. *J. Chem. Phys.* **1991**, *95*, 1635−1647.
(13) Milligan, D. E.; Jacox, M. E. Infrared Spectrum and Structure of Intermediates in the Reaction of OH with CO. *J. Chem. Phys.* **1971**, *54*, 927−942.
(14) Jacox, M. E. The Vibrational Spectrum of the t-HOCO Free Radical Trapped in Solid Argon. *J. Chem. Phys.* **1988**, *88*, 4598−4607.
(15) Petty, J. T.; Moore, C. B. Transient IR Absorption Spectrum of the ν_1 Fundamental of t-HOCO. *J. Mol. Spectrosc.* **1993**, *161*, 149−156.
(16) Sears, T. J.; Fawzy, W. M.; Johnson, P. M. Transient Diode Laser Absorption Spectroscopy of the ν_2 Fundamental of *trans*-HOCO and DOCO. *J. Chem. Phys.* **1992**, *97*, 3996−4007.
(17) Jacox, M. E. *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*; Journal of Physical and Chemical Reference Data, Monograph 3; American Chemical Society: Washington, DC, 1994.
(18) Jacox, M. E. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules. Supplement A. *J. Phys. Chem. Ref. Data* **1998**, *27*, 115−393.
(19) Byrd, E. F. C.; Sherrill, C. D.; Head-Gordon, M. Theoretical Prediction of Molecular Radical Species: A Systematic Study of Equilibrium Geometries and Harmonic Vibrational Frequencies. *J. Phys. Chem. A* **2001**, *105*, 9736−9747.
(20) Ballik, E. A.; Ramsay, D. A. The $A'\ ^3\Sigma_g^- - X'\ ^3\Pi_u$ Band System of the C_2 Molecule. *Astrophys. J.* **1963**, *137*, 61−83.
(21) Milligan, D. E.; Jacox, M. E.; Abouaf-Marguin, L. Vacuum Ultraviolet Photolysis of Acetylene in Inert Matrices. Spectroscopic Study of the Species C_2. *J. Chem. Phys.* **1967**, *46*, 4562−4570.
(22) Jacox, M. E. Matrix Isolation Study of the Vibrational Spectrum and Structure of HC_2. *Chem. Phys.* **1975**, *7*, 424−432.
(23) Shepherd, R. A.; Graham, W. R. M. FTIR Study of D and ^{13}C Substituted C_2H in Solid Argon. *J. Chem. Phys.* **1987**, *86*, 2600−2605.
(24) Jacox, M. E.; Olson, W. B. The $\tilde{A}\ ^2\Pi - \tilde{X}\ ^2\Sigma^+$ Transition of HC_2 Isolated in Solid Argon. *J. Chem. Phys.* **1987**, *86*, 3134−3142.
(25) Kanamori, H.; Hirota, E. Vibronic Bands of the CCH Radical Observed by Infrared Diode Laser Kinetic Spectroscopy. *J. Chem. Phys.* **1988**, *89*, 3962−3969.
(26) Kawaguchi, K.; Amano, T.; Hirota, E. Infrared Diode Laser Spectroscopy of the $\nu_2 + \nu_3$ Band of CCH. *J. Mol. Spectrosc.* **1988**, *131*, 58−65.
(27) Forney, D.; Jacox, M. E.; Thompson, W. E. The Infrared and Near Infrared Spectra of HCC and DCC Trapped in Solid Neon. *J. Mol. Spectrosc.* **1995**, *170*, 178−214.
(28) Peric, M.; Peyerimhoff, S. D.; Buenker, R. J. Ab Initio Investigation of the Vibronic Structure in the C_2H Spectrum: Calculation of Vibronic Energies and Wavefunctions for Various Isotopomers. *J. Mol. Spectrosc.* **1990**, *148*, 180−200.
(29) Hsu, Y.-C.; Shiu, Y.-J.; Lin, C.-M. Laser-Induced Fluorescence Spectroscopy of CCH ($\tilde{X}\ ^2\Sigma^+$) in Vibrationally Excited Levels up to 4500 cm^{-1}. *J. Chem. Phys.* **1995**, *103*, 5919−5930.
(30) Tokaryk, D. W. Presented at the 58th International Symposium on Molecular Spectroscopy, Columbus, OH, 2003; Paper RG05.
(31) Tarroni, R.; Carter, S. Theoretical Calculation of Vibronic Levels of C_2H and C_2D to 10 000 cm^{-1}. *J. Chem. Phys.* **2003**, *119*, 12878−12889.
(32) Herzberg, G.; Lagerqvist, A. A New Spectrum Associated with Diatomic Carbon. *Can. J. Phys.* **1968**, *46*, 2363−2373.
(33) Milligan, D. E.; Jacox, M. E. Studies of the Photoproduction of Electrons in Inert Solid Matrices. The Electronic Spectrum of the Species C_2^-. *J. Chem. Phys.* **1969**, *51*, 1952−1955.
(34) Lineberger, W. C.; Patterson, T. A. Two-Photon Photodetachment Spectroscopy: The $C_2^-\ ^2\Sigma$ States. *Chem. Phys. Lett.* **1972**, *13*, 40−44.
(35) Forney, D.; Althaus, H.; Maier, J. P. An Electronic Absorption Spectrum of C_2^+: $B\ ^4\Sigma_u^- \leftarrow X\ ^4\Sigma_g^-$. *J. Phys. Chem.* **1987**, *91*, 6458−6461.
(36) Maier, J. P.; Rösslein, M. The $B\ ^4\Sigma_u^- - X\ ^4\Sigma_g^-$ Electronic Spectrum of C_2^+. *J. Chem. Phys.* **1988**, *88*, 4614−4620.
(37) Weltner, W., Jr.; Van Zee, R. J. Carbon Molecules, Ions, and Clusters. *Chem. Rev.* **1989**, *89*, 1713−1747.
(38) Hayhurst, A. N.; Kittelson, D. B. The Positive and Negative Ions in Oxy-Acetylene Flames. *Combust. Flame* **1978**, *31*, 37−51.
(39) Jacox, M. E.; Thompson, W. E. The Vibrational Spectra of Molecular Ions Isolated in Solid Neon. I. CO_2^+ and CO_2^-. *J. Chem. Phys.* **1989**, *91*, 1410−1416.
(40) Kawaguchi, K.; Yamada, C.; Hirota, E. Diode Laser Spectroscopy of the CO_2^+ ν_3 Band Using Magnetic Field Modulation of the Discharge Plasma. *J. Chem. Phys.* **1985**, *82*, 1174−1177.
(41) Thompson, W. E.; Jacox, M. E. The Vibrational Spectra of CO_2^+, $(CO_2)_2^+$, CO_2^-, and $(CO_2)_2^-$ Trapped in Solid Neon. *J. Chem. Phys.* **1999**, *111*, 4487−4496.

(42) Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Oka, T. Infrared Spectra of Carboions. II. ν_3 Band of $C_2H_2^+$ ($^2\Pi_u$). *J. Chem. Phys.* **1987**, *86*, 3755−3756.

(43) Forney, D.; Jacox, M. E.; Thompson, W. E. The Vibrational Spectra of Molecular Ions Isolated in Solid Neon. VIII. $HCCH^+$ and HCC^-. *J. Mol. Spectrosc.* **1992**, *153*, 680−691.

(44) Forney, D.; Jacox, M. E.; Lugez, C. L.; Thompson, W. E. Matrix Isolation Study of the Interaction of Excited Neon Atoms with Allene and Propyne: Infrared Spectra of $H_2CCCH_2^+$ and H_2CCCH^-. *J. Chem. Phys.* **2001**, *115*, 8418−8430.

(45) Craig, N. C.; Pranata, J.; Reinganum, S. J.; Sprague, J. R.; Stevens, P. S. Vibrational Spectra of $C_3H_3^+$, $C_3D_3^+$, $C_3H_2D^+$, and $C_3D_2H^+$ and Force Constants for This Ion System. *J. Am. Chem. Soc.* **1986**, *108*, 4378−4386.

(46) Frenking, G.; Schwarz, H. Ab Initio Molecular Orbital Calculations on the Interconversion of Allene and Propyne Cation Radicals and the Mechanism for Hydrogen Loss from $C_3H_4^+$. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 131−138.

(47) Forney, D.; Jacox, M. E.; Thompson, W. E. The Infrared Spectra of *t*-HOCO, $HCOOH^+$, and HCO_2^- Trapped in Solid Neon. *J. Chem. Phys.* **2003**, *119*, 10814−10823.

(48) Bell, S.; Ng, T. L.; Walsh, A. D. Vacuum Ultraviolet Spectra of Formic and Acetic Acids. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 393−401.

(49) Schwell, M.; Leach, S.; Hottmann, K.; Jochims, H.-W.; Baumgärtel, H. He I Photoelectron Spectroscopy of Formic Acid Isotopomers HCOOH and DCOOD. *Chem. Phys.* **2001**, *272*, 77−90.

(50) Leach, S.; Schwell, M.; Talbi, D.; Berthier, G.; Hottmann, K.; Jochims, H.-W.; Baumgärtel, H. He I Photoelectron Spectroscopy of Four Isotopologues of Formic Acid: HCOOH, HCOOD, DCOOH, and DCOOD. *Chem. Phys.* **2003**, *286*, 15−43.

(51) Jacox, M. E.; Thompson, W. E. Infrared Spectra of $HOCO^+$ and of the Complex of H_2 with CO_2^- Trapped in Solid Neon. *J. Chem. Phys.* **2003**, *119*, 10824−10831.

(52) Kidd, K. G.; Mantsch, H. H. Formate Anion: The Physical Force Field. *J. Mol. Spectrosc.* **1981**, *85*, 375−389.

(53) Botschwina, P. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; p 100.

(54) Pelc, A.; Sailer, W.; Scheier, P.; Probst, M.; Mason, N. J.; Illenberger, E.; Märk, T. D. Dissociative Electron Attachment to Formic Acid (HCOOH). *Chem. Phys. Lett.* **2002**, *361*, 277−284.

(55) Amano, T.; Tanaka, K. Difference Frequency Laser Spectroscopy of the ν_1 Band of $HOCO^+$. *J. Chem. Phys.* **1985**, *82*, 1045−1046.

(56) Amano, T.; Tanaka, K. Difference Frequency Laser Spectroscopy of the ν_1 Fundamental Band of $HOCO^+$. *J. Chem. Phys.* **1985**, *83*, 3721−3728.

(57) Dopfer, O.; Olkhov, R. V.; Roth, D.; Maier, J. P. Intermolecular Interaction in Proton-Bound Dimers. Infrared Photodissociation Spectra of Rg-$HOCO^+$ (Rg = He, Ne, Ar) Complexes. *Chem. Phys. Lett.* **1998**, *296*, 585−591.

(58) Nizkorodov, S. A.; Dopfer, O.; Ruchti, T.; Meuwly, M.; Maier, J. P.; Bieske, E. J. Size Effects in Cluster Infrared-Spectra − The ν_1 Band of Ar_n-HCO^+ (n=1−13). *J. Phys. Chem.* **1995**, *99*, 17118−17129.

(59) Ruscic, B.; Litorja, M. Photoionization of HOCO Revisited: A New Upper Limit to the Adiabatic Ionization Energy and Lower Limit to the Enthalpy of Formation. *Chem. Phys. Lett.* **2000**, *316*, 45−50.

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