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# Formation of Hydrocarbons from Carbon Monoxide on Rhodium/Alumina Model Catalysts

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When tunnel junctions containing carbon monoxide adsorbed on alumina-supported Rh are heated in hydrogen the vibrational peaks due to carbon monoxide decrease and a new set of vibrational peaks grows. Shifts in the positions of some of these new peaks are observed if the normal $^{12}C^{16}O$ is replaced by $^{13}C^{16}O$, but not if it is replaced by $^{12}C^{18}O$. This suggests that the new surface species includes the carbon from the CO, but not the oxygen. The set of new peaks grows together and is in one-to-one correspondence with the peaks of ethylidene as extrapolated between published spectra of halogenated derivatives. A different surface species, tentatively identified as formate ions, can be produced by heating without hydrogen.

## I. INTRODUCTION

The observation of catalytic intermediates on supported metal catalysts would enable one to describe the step-by-step formation of hydrocarbons from carbon monoxide. Many possible intermediates have been proposed (*1*), but there is little spectroscopic information available to enable the determination of the correct reaction pathway for any given catalyst system. This study was carried out with the hope that tunneling spectroscopy (*2*) might give new information about relatively stable surface species present during the hydrogenation of carbon monoxide. This work is a continuation of a previously reported tunneling spectroscopy study (*3, 4*) of a model rhodium/alumina catalyst.

We report the observation of two surface species formed from chemisorbed carbon monoxide. One species appears to be formate ions; the second is a two-carbon, four-hydrogen molecule that is multiply bonded to the surface, $\mu$-ethylidene. These identifications are based on the measurement of isotopic shifts and on comparison of mode positions to known compounds. Evidence for an oxygen-free intermediate in the methanation reaction on W and Ru has come from recent absorbtion studies of simple oxygen-containing molecules: $H_2CO$ (*5*) and $CH_3OH$ (*6*). Palmer and Vroom (*7*) postulated a surface carbon intermediate for methanation over Ni and Co. Recent work with electron energy-loss spectroscopy on the absorption of $C_2H_2$, $C_2D_2$, and $C_2H_4$ on Pt (*8*) and Ni (*9*) has provided valuable vibrational data on two-carbon species adsorbed on metals. A species formed from heating adsorbed ethylene was initially identified as an ethylidene species by Ibach *et al.* (*8*), but has been reidentified by Kesmodel *et al.* (*10*) as an ethylidyne species and by Demuth (*11*) as a vinyl-like species. A basic source of the problem in assigning the vibrational modes in electron energy-loss spectroscopy is the strong orientational selection rule. This introduces an uncertainty in assignments since the orientation of adsorbed species is not known in advance. Thus it is unclear which vibrational modes will be missing. More than one assignment can be consistent with the observed modes since missing modes of a proposed species can be explained by assuming that it has a particular orientation. Hence other data such as LEED (*10*) or

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temperature-programmed thermal desorption (*11*) or uv photoemission spectroscopy (*11*) must be used to argue which of the species consistent with the electron energy-loss data is in fact present.

Fortunately, selection rules in tunneling spectroscopy are present but very weak (*2b*). Typically, all the vibrational modes of simple molecules are seen: both Raman and infrared active, both parallel and perpendicular to the surface (*2b*). In the present work all the vibrational modes of the ethylidene species are seen and there are no extra modes. Specifically, the new set of modes that grows together upon hydrogenation of the adsorbed CO is in one-to-one correspondence with the set of modes for an ethylidene species.

A formate species has been observed with infrared spectroscopy to form on ruthenium/alumina catalysts by others (*12*), and is not thought to be an active intermediate in hydrocarbon synthesis. Although the $\mu$-ethylidene species has not been observed previously on a supported metal catalyst, a similar $\mu$-ethylidene complex $\mu CHCH_3\ [\eta\text{-}C_5H_5Rh(CO)]_2$ has been synthesized by Herrmann *et al.* (*13*). The ethylidene species may possibly be an intermediate for some of the products of Fischer–Tropsch synthesis on rhodium. In a recent study by Bhasin *et al.* (*14*), rhodium/$SiO_2$ catalysts were shown to convert CO to $C_2$ chemicals with a 43% efficiency.

## II. EXPERIMENTAL METHODS

The tunneling junctions used in these experiments are fabricated with a standard geometry; they consist of a thin aluminum film upon which an oxide is grown to form an insulating barrier, a dopant, and a lead top electrode. The details of the fabrication process and measurement techniques can be found in the literature (*2, 15*).

The dopant for these experiments is a small amount of rhodium that is evaporated onto the oxidized aluminum (*16*), and exposed to various gases. Prior to this evaporation the oxide surface (*17*) is usually cleaned in an argon glow discharge (*18*). The rhodium is evaporated under varied vacuum conditions ranging from $3 \times 10^{-6}$ Pa residual gases, mainly hydrogen and water vapor, to $1 \times 10^{-2}$ Pa carbon monoxide. A typical evaporation is one in a pressure of $2 \times 10^{-3}$ Pa of carbon monoxide. The carbon monoxide is left in the vacuum chamber for 60 sec, then pumped out, and the top lead electrode deposited. This top layer of lead is normally 1500 Å thick.

We usually evaporate enough rhodium to equal a 4- to 6-Å uniform layer. The rhodium does not, however, form a uniform layer; instead, it lowers its surface free energy by balling up to form small particles with diameters on the order of 20 to 30 Å (*4*).

The sensitivity of tunneling spectroscopy has been measured by two of the authors (R.M.K. and P.K.H.) (*19*). It was found that 1% of a monolayer of *p*-deuterobenzoate ions could be detected. In this work with supported rhodium, we are forced to deal with lower overall intensities than are produced by an organic monolayer. To aid in the detection of very small peaks, we take differential spectra by subtracting the signal of an undoped junction from the spectrum of a doped junction (*15*). In every experiment, this undoped junction is formed next to the doped junction, so all spectra taken are the difference spectra of two junctions. The simultaneous formation of both junctions reduces subtraction problems associated with the variability of control, or undoped, junctions. When spectra are taken the modulation voltage is equalized near the $Al_2O_3$ phonon, at 117 meV. Since the instrumentation used actively balances only the direct current, the resulting differential spectrum best suppresses the undoped spectra near the $Al_2O_3$ phonon. The background slope is reduced, but not eliminated since the presence of the Rh modifies the conductance vs voltage curve of the junction. The presence of the (nonsuperconducting) Rh also modifies the relatively large structure due to superconducting Pb below 30 meV. The onset of the structure due to cancellation errors between the modified and unmodified superconducting Pb in the junctions with and without Rh is seen as the rise of the beginning of the spectra in this paper and is easily identified as such by its sensitivity to an applied magnetic field.

The modulation voltage used, 2 mV, gives a resolution of 3.9 meV (32 $cm^{-1}$) at 4.2 K (*2*). Peak positions are determined by the method of mean intercepts. Typical sample standard deviations for measured peak positions range from ±0.2 to ±0.4 meV. We note that a resolution of 4 meV in no way implies that peak positions cannot be determined to better than 4 meV. It does mean that we will not resolve two peaks that are separated by less than 4 meV.

For the experiments with isotopes, $^{12}C^{18}O$ (99%) was obtained from Stohler isotopes, and $^{13}C^{16}O$ (90.5%) was obtained from Merck, Sharp, and Dohme. Both were used as received without further purification.

To produce hydrocarbons from the carbon monoxide present in the junctions, the junctions must be heated. At present, our best vacuum is not sufficient to heat an uncompleted junction without exposure to contaminating residual gases. To obtain hydrocarbons without such contamination, we first complete the junctions with a top lead electrode and then heat the completed junctions in a separate chamber. There are advantages and disadvantages inherent in heating completed junctions in a separate chamber. The main disadvantage is that it removes our model supported metal system another step from straightforward comparison to practical catalyst systems. The main advantage is that we can take spectra before and after we heat the junctions, and we can take successive spectra of the same junction after heating to increasing temperature. There is also the possibility that our observed lack of hydrocarbon contamination despite exposure of completed junctions to room air is due to a filter effect of the lead, i.e., letting small reactants such as hydrogen through while screening out contamination from large hydrocarbons. Jaklevic and Gaerttner (*20*) have begun studying the diffusion of various molecules through the top lead electrode. This type of work may lead to a better understanding of the filtering characteristics of the lead.

To produce hydrocarbon spectra with good peak intensities we place a completed pair of junctions, one doped with rhodium evaporated in carbon monoxide and one undoped, in a small high-pressure cell. We evacuate the cell, and then pressurize it with hydrogen and carbon monoxide. For the experiments with isotopes hydrogen alone is used. We use maximum tank pressure, typically $1 \times 10^7$ Pa. The effective pressure of gas present on the rhodium is not known. The cell is then heated to 380–450 K for 20 to 60 min to form the hydrocarbons. After cooling, the junction is removed and immersed in liquid helium to obtain a spectrum.

## III. RESULTS

Figure 1 shows the differential spectra that results from heating a completed pair of junctions to 420 K in $1 \times 10^7$ Pa of hydrogen. No hydrocarbon was observed to form on the junction without rhodium. Seven modes of this new species are labeled by number in Fig. 1. This hydrocarbon forms at temperatures as low as 380 K and appears to desorb or react at temperatures higher than 450 K.

To aid in the identification of this species, isotopic substitution of the carbon monoxide was used. Figure 2 compares the spectra for this hydrocarbon that results from the use of $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{12}C^{16}O$ in the region 125 meV (~1000 $cm^{-1}$) to 190 meV (~1530 $cm^{-1}$). Isotopic shifts can be seen with $^{13}C^{16}O$. No shifts in the hydrocarbon peaks are seen with $^{12}C^{18}O$. This lack of measureable shifts with $^{12}C^{18}O$ is important. Many proposed intermediates involve a carbon–oxygen bond of some type (*21*, *22*).

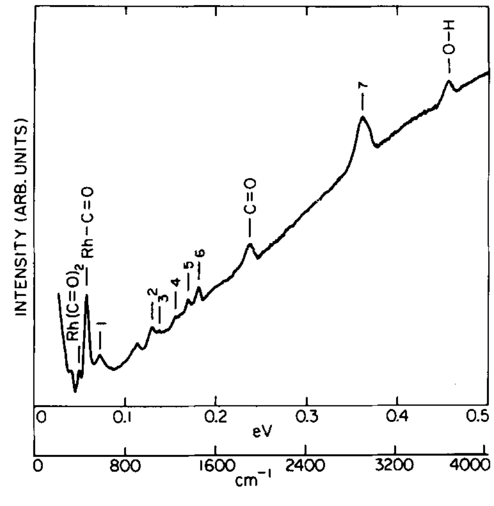

FIG. 1. Differential spectra of $^{13}CO$ on rhodium/alumina that has been heated to 420 K in hydrogen. Modes due to hydrocarbon formation are numbered 1 to 7. By comparison to published infrared and Raman spectra the hydrocarbon is identified as an ethylidene species.

The group —CH=O, one possible intermediate, would have a carbon–oxygen mode between 190 and 220 meV (ν-CH=O) that is not seen. Such a carbon–oxygen bond formed from the carbon monoxide would have an easily observed isotope shift with $^{12}C^{18}O$ of 3 to 4 meV (*23*). Other oxygenated species, such as $-CH_2OH$ would also have an isotope shift large enough to be seen in the carbon–oxygen mode (*23*). We are not observing an oxygenated hydrocarbon. No mode in the region 125 to 180 meV shifts with the use of $^{12}C^{18}O$. (In contrast, the modes of the adsorbed $^{12}C^{18}O$ itself have definite shifts (*4*).)

One remaining possibility that is not excluded by the lack of shifts is that oxygen from the surface, for example, from the OH groups on the alumina support, is incorporated into the structure. We believe that this is unlikely, based on the agreement of the observed mode positions with a hydrocarbon to be discussed below and on the lack of agreement with the many possible oxygen-containing species that we have examined. We cannot, however, rule out a small concentration (≤20%) of any species. We can only identify the dominant species.

The lack of intensity makes precise measurements of most of the observed shifts with $^{13}C^{16}O$ difficult. Uncertainties in shift magnitudes are large enough to prevent mode assignments without reference to additional data. However, all shifts measured are consistent with the mode assignments we make and are discussed individually below.

The presence of the mode at 170.8 ± 0.2 meV, mode 5 in Fig. 1, is characteristic of a methyl group bonded to another carbon atom. This mode is the symmetric deformation of a $CH_3$ group, and is sensitive to the bonding of the carbon atom. With $^{13}C$ substitution this mode is expected to downshift about 1.0 meV (*24*). We measure $-1.4 \pm 0.4$ meV (see Fig. 2). The mode at 181.4 ± 0.2 meV, mode 6 in Fig. 1, is then identified as the antisymmetric deformation of the $CH_3$ group. Its expected shift is $-0.7$ meV (*24*). We observe a shift of $-0.4 \pm 0.4$. The only other CH species with a vibration in this position is the $CH_2$ group. We do not see a complete set of modes due to a $CH_2$

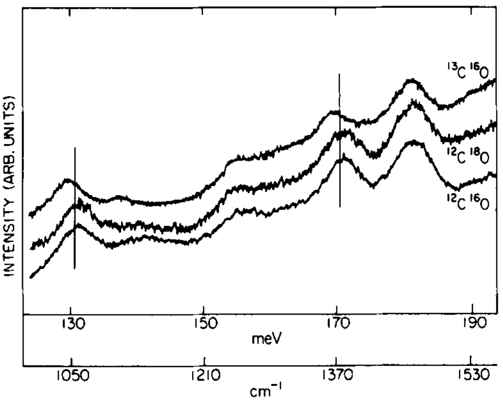

FIG. 2. Spectra resulting from the use of $^{12}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{16}O$ are shown in the region from 125 to 190 meV. No shifts in the hydrocarbon spectra are seen with the use of $^{12}C^{18}O$. Shifts are observed with the use of $^{13}C^{16}O$. This suggests that these hydrocarbon modes involve the carbon but not the oxygen from the chemisorbed CO. The reference line drawn through the peak at 170.8 ± 0.2 meV ($^{13}C^{16}O$) is drawn at 170.6 meV, the lower limit of its measured position. An isotope shift is still clearly visible in the $^{13}C^{16}O$ spectrum in this mode.

group; we do see other modes due to a $CH_3$ group. There is no other CH group that will have modes in this region, and the isotope shift measurements do not allow the assignment of either of these modes as carbon–carbon or carbon–oxygen modes. Thus there is little doubt about the assignments of modes 5 and 6.

Since the hydrocarbon contains a $CH_3$ group, there is only one possible one-carbon species, $RhCH_3$. Figure 3 shows a comparison of some mode positions of $X$–$CH_3$ for $X$ = bromine and iodine (*25*) with the species of Fig. 1. The mode positions for the three species have been displaced by the inverse root of the mass of $X$. It can be seen that the species $X$-$CH_3$ has too few modes to be correct. The two modes that do agree are modes 1 and 6. Mode 1 is in the position for a Rh–C bond. Mode 6, the asymmetric deformation of a $CH_3$ group, is known to be insensitive to the bonding of the carbon atom; thus this agreement is expected. As mentioned previously, mode 5 is sensitive to the bonding of the carbon atom; it is seen to be downshifted in Fig. 3 for both bromine (1332 $cm^{-1}$) and iodine (1276 $cm^{-1}$) species.

The possible two-carbon species that contain a $CH_3$ group are: (a) $RhCH_2CH_3$, (b) $Rh_2CHCH_3$, and (c) $Rh_3CCH_3$. The three-hydrogen species, (c), does not have enough CH modes between 100 meV (800 $cm^{-1}$) and 200 meV (1600 $cm^{-1}$) to be the correct species. The five-hydrogen species, (a), is represented in Fig. 3 by $XCH_2CH_3$ for $X$ = bromine and iodine (*26*). This molecule correctly matches modes 5 and 6 which are due to the terminal $CH_3$ group. But the modes due to the $CH_2$ group, as mentioned previously, are absent. Specifically, we do not observe a mode near 92 meV (790 $cm^{-1}$). This species also has too few modes between 100 and 200 meV. The four-hydrogen species, (b), is represented in Fig. 3 by $X_2$ $CHCH_3$ for $X$ = bromine and iodine (*27*). It is seen that the modes agree in both number and position. (Complete mode assignments and approximate descriptions of

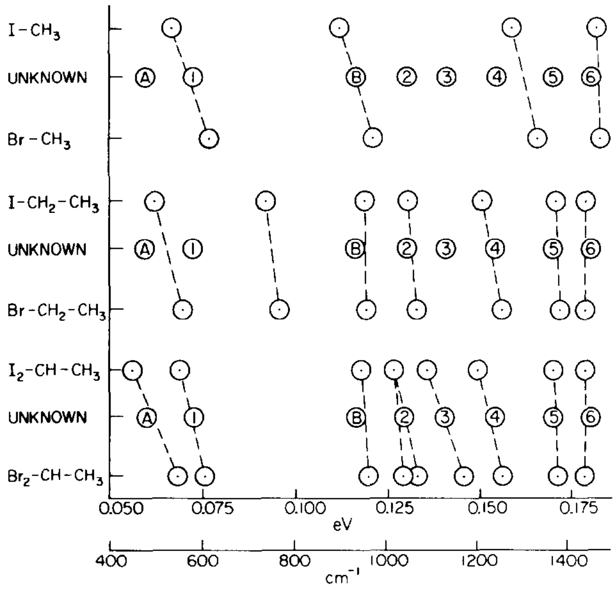

FIG. 3. Comparisons are shown between mode positions of the unknown hydrocarbon and positions from the literature (*17–19*) of known compounds. The vertical axis is scaled by the inverse square root of the mass of bromine, rhodium, and iodine. It is displaced for each set of compounds. Modes 1 to 6 of the unknown are observed directly. The measurement of the positions of modes A and B is difficult due to overlap with other modes present. From the agreement with the two ethylidene species, the unknown hydrocarbon is identified as a $\mu$-ethylidene species.

the modes of $Br_2CHCH_3$ have been published by Durig *et al.* (*27d*).)

Table 1 provides a detailed comparison. Perfect agreement in mode positions is not expected since: (i) we have not made any corrections for bonding differences between a halogen and rhodium atom. Such corrections are expected to be small since the force constants involved are: C–Br (*27d*), 181 ± 10 N/m; C–I (*26c*), 191 ± 26 N/m; and C–Rh (*4*), approx 200 N/m. (ii) There should be downshifts in the range 0.1 to 1% from image dipoles in the top lead electrode (*28*) and upshifts of the order of 0.7 meV from the superconducting energy gap (*28*). We have not attempted to correct the data for either of these shifts.

Two modes labeled A and B and shown in Fig. 3 are not numbered in Fig. 1. The lowest of these at 60 meV, mode A, is not numbered due to the presence of the RhCO bending mode near 58.1 meV ($^{12}C^{16}O$) upshifted 1.5 meV. This upshift increases with subsequent heating of the junctions. The growth of a new peak near 60 meV due to the formation of the hydrocarbon could explain this shift. The second mode of Fig. 3 that is not numbered, mode B, is the mode at 113 meV in Fig. 1 ($^{13}C^{16}O$). We are unable to measure this mode position very accurately due to interference from the very strong aluminum oxide mode at 117 meV. Subtraction errors lead to baseline shifts of the same order of magnitude as this peak. As a result of this interference, the average isotope shift measured, 3 meV, has been assigned a large uncertainty, ±3 meV. A carbon–carbon bond would be expected to downshift about 4 meV in this molecule.

TABLE 1

Comparison of Frequencies

| $CH_3CHBr_2$[27a] | $CH_3CHI_2$[27a] | Calculated[b] | Surface species[c] |
|---|---|---|---|
| 21.3 | 14.1 | 17.2 | Not accessible |
| 35.1 | 29.8 | 32.1 | Not accessible |
| 42.5 | 36.5 | 39.0 | 41.2 ± 0.4 |
| 67.8 | 57.8 | 62.0 | 60 ± 1.5 |
| 75.6 | 68.4 | 71.5 | 73.6 ± 0.4 |
| 119.8 | 117.3 | 118.4 | 117 ± 2 |
| $\begin{pmatrix}129.1\\133.3\end{pmatrix}$ | 129.0 | $\begin{pmatrix}129.0\\130.8\end{pmatrix}$ | 131.2 ± 0.5 |
| 145.3 | 136.3 | 140.1 | 141 ± 1 |
| 155.9 | 152.1 | 153.7 | 155 ± 1 |
| 171.5 | 170.1 | 170.7 | 170.8 ± 0.2 |
| 178.9 | 177.7 | 178.2 | 181.4 ± 0.2 |
| 363.4 | 360.1 | 361.5 | 361.5 ± 1 |
| $\begin{pmatrix}369.4\\371.0\end{pmatrix}$ | 367.6 | $\begin{pmatrix}368.4\\369.1\end{pmatrix}$ | 367.5 ± 1 |
| 374.0 | Not resolved | — | Not resolved |

[a] Raman (liquid) frequencies. Infrared frequencies vary up to ±1 meV from Raman frequencies.

[b] From hydrogenation of $^{12}C^{16}O$.

[c] Calculated from $\omega = \omega_{\mathrm{I}} + (\omega_{\mathrm{Br}} - \omega_{\mathrm{I}})\ \{[(102.9)^{-1/2} - (126.9)^{-1/2}]/[(79.9)^{-1/2} - (126.7)^{-1/2}]\}$. We note $K_{\mathrm{C-Br}} \simeq K_{\mathrm{C-I}} \simeq K_{\mathrm{C-Rh}}$.

There is one last mode in Fig. 1 that is not numbered or labeled. This mode is at 41.2 ± 0.4 meV for junctions doped with $^{12}C^{16}O$ and $^{12}C^{18}O$. It downshifts to 40.2 ± 0.4 meV with $^{13}C^{16}O$. The molecule $I_2CHCH_3$ has a mode at 36.5 meV and $Br_2CHCH_3$ has a mode at 42.5 meV (*27*). The inverse-square root scaling used in Fig. 3 would thus place this mode at 39.0 meV. In $Br_2CHCH_3$ this mode has been assigned as due to $CBr_2$ wag and $CBr_2$ symmetric stretch (*27d*). Thus it would be expected to be one of the most sensitive to differences between a carbon–halogen and carbon–rhodium bond.

Molecules with more than two carbon atoms have, in general, too many modes to be the correct species. One exception to this is the three-carbon species $(CH_3)_2CH\text{-}X$ (*29*). The degeneracy of the $CH_3$ modes, only slightly split, yields a spectrum with the correct number of strong modes in the region 100 to 200 meV (800 to 1600 $cm^{-1}$). Mode position agreement, however, is weakened for CH modes 3 and 4, reflecting the change in bonding of this carbon atom. Mode position agreement is lost entirely for both mode 1 and the hydrocarbon mode at 117 meV ($^{12}C^{16}O$) reflecting the additional mass of the second $CH_3$ group. Thus we conclude that we are not seeing molecules with more than two carbon atoms.

To summarize our identification: (i) The lack of shifts with $^{12}C^{18}O$ and the lack of some characteristic modes suggest that the unknown does not contain oxygen. (ii) A detailed comparison of observed peak positions for the unknown with all possible one-, two-, and three-carbon species shows agreement only for $X_2CHCH_3$. Measured

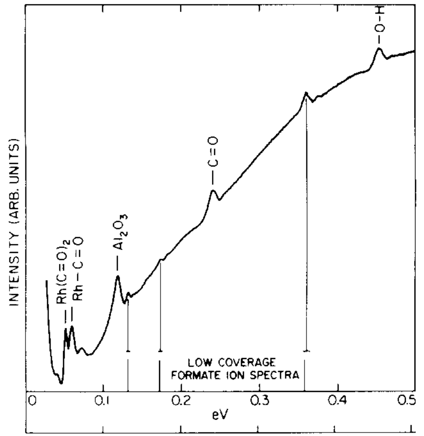

FIG. 4. Differential spectra of CO on rhodium/alumina that has been heated to 440 K with out hydrogen. This temperature is not sufficient to reduce the ethylidene mode intensities by desorption or reaction, but the ethylidene modes that appear are much less intense than for similar junctions heated in $H_2$. In addition, the intensity of modes at 131 and 365 meV are too large to be due to only the ethylidene species. A new mode has also appeared near 173 meV. From the comparison shown to low coverage formate ion spectra, this new species is tentatively identified as formate ions.

isotope shifts with $^{13}C^{16}O$ are consistent with this identification. (3) The agreement with the expected ethylidene modes is, to within our 4-meV resolution, perfect in number, and calculated mode positions all lie within the observed widths of all modes. This agreement is listed in Table 1.

## IV. DISCUSSION

The identification of a molecule by the assignment of its vibrational spectrum is a difficult task. Our identification of an ethylidene species is based on the observation of spectra from over 30 separate experiments that produced hydrocarbons. An important part of any structural identification is that all of the modes assigned to the same species must correlate in intensity. In these experiments we have observed this required uniform growth of the ethylidene modes for junctions heated in a $H_2$ atmosphere.

For junctions heated without exposure to $H_2$ we observe a change in the relative intensities of the modes near 131 and 360 meV with respect to the majority of the proposed ethylidene modes. In addition, we observe a new mode at 172.5 ± 0.8 meV. Figure 4 shows the differential spectra of a sample heated to 400K without $H_2$. The ethylidene species is present in smaller amounts than is typical for similar junctions heated in $H_2$. (This temperature is not sufficient to reduce the intensity of the ethylidene modes.) The three lines in the figure are at the positions of the modes first visible in the low-coverage formate ion spectrum obtained in tunneling experiments by Lewis *et al.* (*30*). The similarity in peak positions suggests that the three modes in our spectrum may be due to a low coverage of formate ions. We do not know if the ions are bonded to rhodium, or alumina, or both.

The formation of formate ions on a supported metal catalyst has been observed previously. In experiments by Dalla Betta and Shelef (*12*), formate ions were observed to form on a ruthenium/alumina catalyst. In a transmission infrared study with isotopes, they observed that the formate species was an inactive reaction product.

The source of hydrogen for the formation of hydrocarbons in this experiment without $H_2$ is not understood. Possible sources are the OH groups in the junctions and water vapor in the heating cell. Water molecules have been found to easily penetrate the Pb overlayer (*20*). We found that deuteration of the OH groups present in the junction produced a deuterated hydrocarbon. In any case, we note that junctions heated in $H_2$ form more hydrocarbon than junctions heated without $H_2$. As noted before, we cannot rule out a small concentration (≤20%) of any species. We can only identify the dominant species.

Another possibility is that there are more than one species with comparable concentrations that combine to give the observed group of vibrational modes. This seems unlikely since: (i) they would have to form with nearly identical kinetics so that the entire group of modes would grow uniformly; (ii) they would have to have unobserved modes since, as discussed above, other hydrocarbons have modes in positions where we do not observe modes. Missing modes are uncommon in tunneling spectroscopy because of the relatively weak selection rules (*31, 32*). For example, in recent experiments on sulfonate ions of known orientation all the infrared and Raman active modes appeared with comparable intensities (*33*). The modes with oscillating dipole moments parallel to the surface were reduced in intensity relative to the modes with oscillating dipole moments perpendicular to the surface, but only by a factor of the order of 2.

In summary, a group of vibrational modes that is in one-to-one correspondence in number and position with the modes of ethylidene grows uniformly when a model rhodium on alumina catalyst with adsorbed CO is heated in $H_2$. The most probable explanation is that ethylidene species are formed from the hydrogenation of the adsorbed carbon monoxide.

We could only speculate whether this species is dominant (or even present) on an actual rhodium/alumina catalyst during hydrocarbon synthesis. Our experiments have suggested, however, that this is a relatively stable surface species that is a good candidate for a reaction intermediate for some of the products of hydrocarbon synthesis.

## ACKNOWLEDGMENTS

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