FTIR Spectroscopy of Cyclic TiC_3 in Solid Ar

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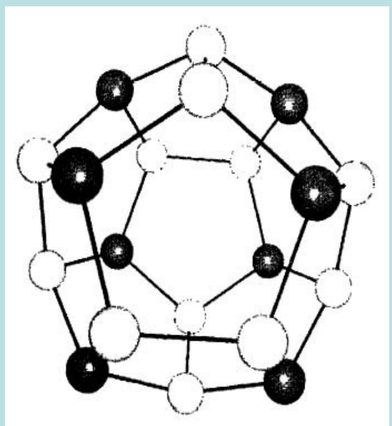
Abstract

The FTIR (Fourier transform infrared) spectrum of TiC_3 was observed by trapping the vapor produced during dual Nd:YAG laser ablation of Ti and C rods in a solid Ar at ~10 K. Measurements of frequencies and ^{13}C isotopic shifts have enabled the identification of the fan-like (C_{2v}) isomer of TiC_3 with vibrational fundamentals $\nu_3(a_1)$ = 624.3 and $\nu_5(b_2)$ = 1484.2 cm^{-1}. A third fundamental $\nu_4(b_1)$, has been tentatively identified at 573.8 cm^{-1}. The results are in good agreement with the predictions of DFT (density functional theory) calculations at the B3LYP/6-311G(3*df*, 3*pd*) level. The observed C_{2v} structure and observed ν_3 metal-carbon stretching mode are also consistent with earlier results from photoelectron spectroscopy. Small molecules composed of a transition metal attached to carbon chains (such as TiC_3) are of interest because they may serve as fundamental building blocks of larger 'metcar' structures; they also have the potential to be observed in interstellar space and circumstellar shells.

Background

Metallocarbohedrenes

- Metallocarbohedrenes, such as Ti_8C_{12}, are very stable, closed structures containing carbon and metal atoms. An example is shown at right, in which C and Ti are represented by white and black spheres, respectively.
- Smaller 'metcar' structures such as TiC_2 or TiC_3 may be possible building blocks for larger metcars.



Astrophysical

- Carbon chains have been detected in stars. Additionally, spectral features from molecules containing transition metals have also been detected in stars, particularly M-type stars. Therefore, it is feasible that 'metcars' may be found in stars.
- Experimental determination of 'metcar' spectra is necessary before these molecules can be found in space.

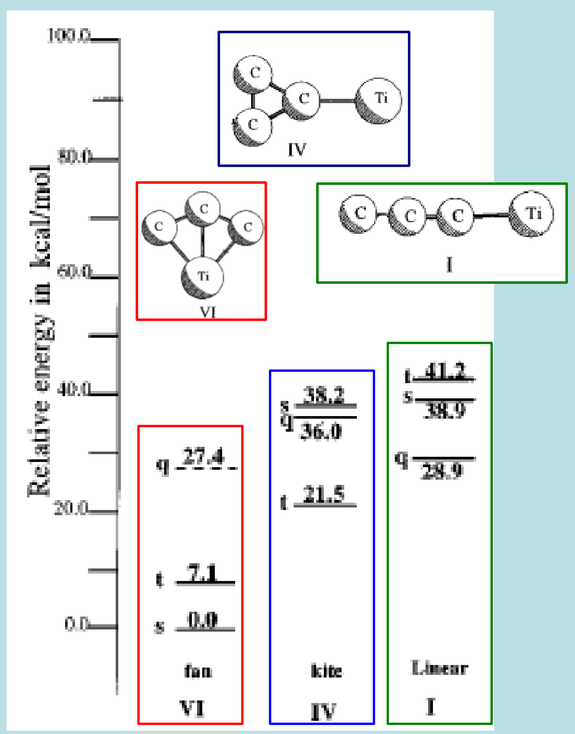
Experimental

- Wang, *et al.*(1997) observed some vibrational modes for TiC_n, n = 2-5 using photoelectron spectroscopy (PES). Their observations are displayed in the table at right.
- Ring-like structures were proposed for these molecules based on comparison to previous LaC_n and YC_n studies.
- The uncertainty (30 – 60 cm^{-1}) of their results is large and makes this data unsuitable for astrophysical detection of these molecules.

TiC_2	560 ± 50 cm^{-1}
TiC_3	650 ± 30 cm^{-1}
TiC_4	440 ± 40 cm^{-1}
TiC_5	240 ± 60 cm^{-1}

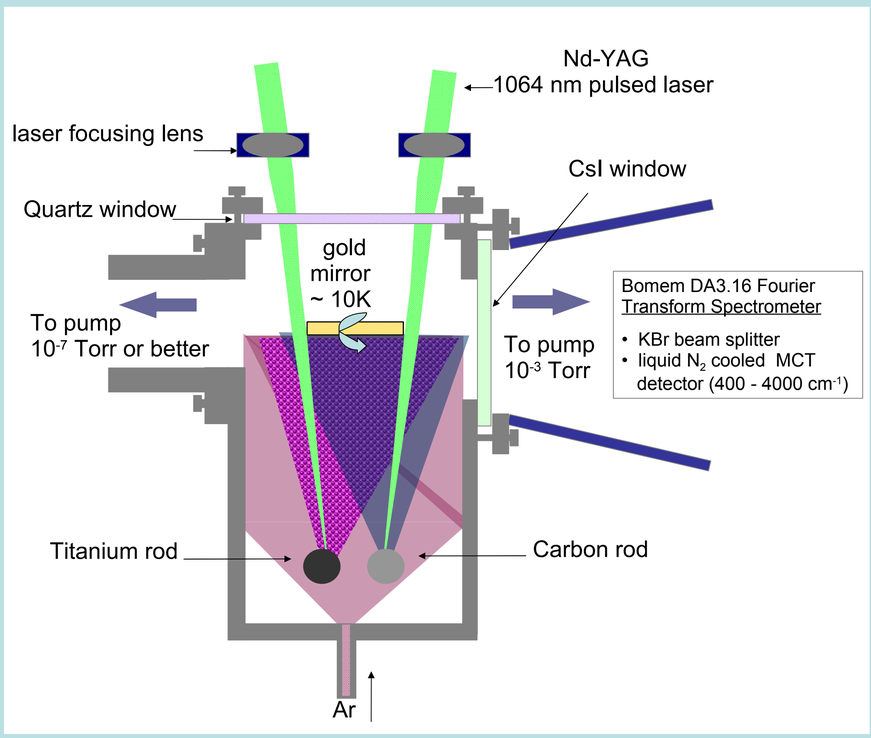
Theoretical

- Sumathi and Hendrickx (1998) published DFT calculations at the B3LYP level for several isomers (structures) of TiC_n, n = 2 - 4.
- Vibrational frequencies and electronic states were calculated for all isomers considered. The three most energetically favored structures of TiC_3 are shown at right.
- The energy level diagram indicates that the "fan" (VI) structure is energetically favored over the "kite" (IV) and linear (I) structures.



Experimental Procedures

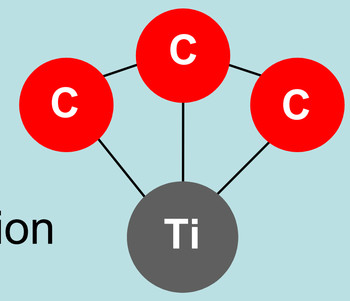
- Two Nd:YAG lasers ablate the surfaces of Ti and C rods. Molecules formed in the resulting vapor are trapped in an Ar matrix on the surface of the gold mirror (see figure at right).
- The mirror is rotated towards the spectrometer and an absorption spectrum is taken.
- Annealing the sample sharpens spectral lines, diminishes secondary trapping sites, and creates larger molecules from smaller ones.
- Identification of a molecule *requires* observing the isotopic shifts produced when a ^{13}C is substituted for a ^{12}C in the molecule in addition to comparison to a theoretical simulation.
- Different variables affecting the matrix sample, such as C rod composition and ablation rates of the rods, are adjusted over several experiments.



Results & Analysis

Theoretical Predictions

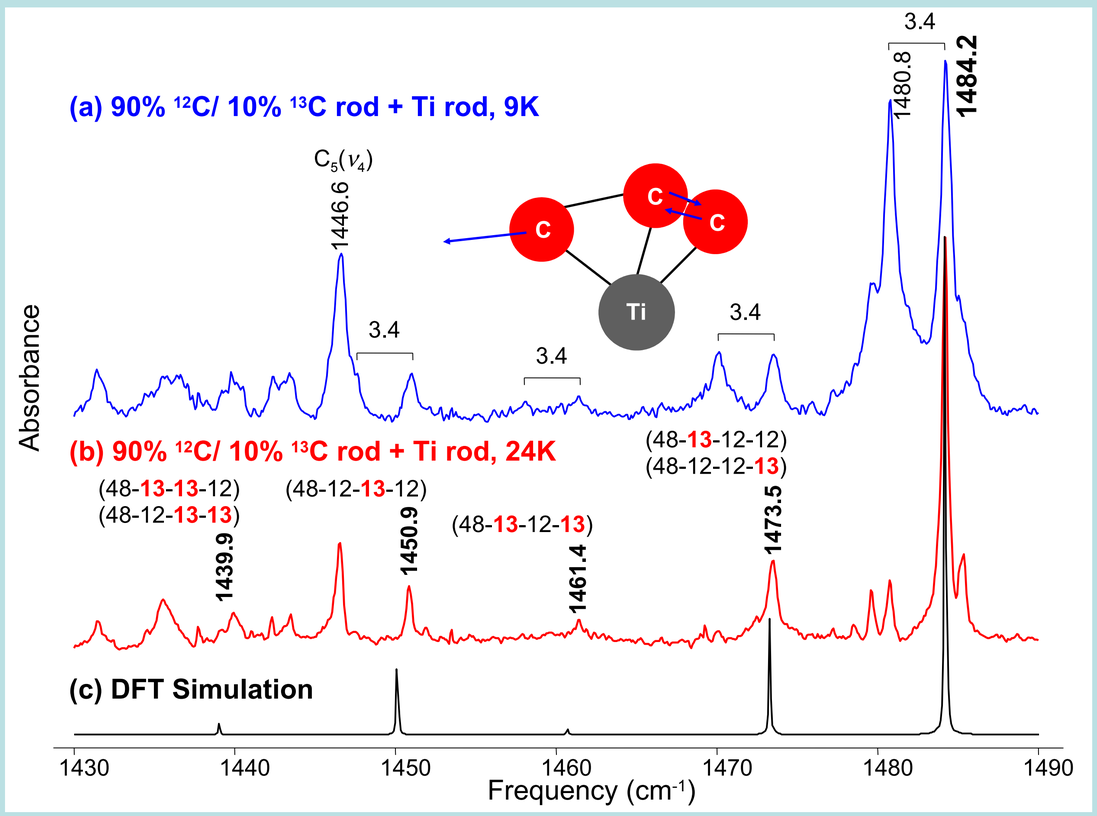
- The table at left shows the calculated frequencies and intensities for the six modes of the fan-like isomer of TiC_3 as predicted by Rittby (2006).
- The ν_1 and ν_2 modes are likely too weak to be observed. The ν_6 mode, though strong, falls outside of the observation range.
- The calculated ν_3 frequency is in good agreement with the 650 ± 50 cm^{-1} observed by Wang, *et al*.



Vibrational mode	Frequency (cm^{-1})	Infrared intensity (km/mole)
$\nu_1(a_1)$	1291.1	4.1
$\nu_2(a_1)$	865.5	4.6
$\nu_3(a_1)$	696.7	64.4
$\nu_4(b_1)$	620.5	11.6
$\nu_5(b_2)$	1549.4	39.3
$\nu_6(b_2)$	459.8	28.2

ν_5 fundamental

- Spectrum (a) of the figure below shows an *unannealed* spectrum for the sample. The fundamental is observed at 1484.2 cm^{-1} with a strong satellite absorption 3.4 cm^{-1} to the left at 1480.8 cm^{-1} which results from a secondary trapping site.
- Isotopic shifts separated by 3.4 cm^{-1} are visible for both the fundamental and satellite.
- Spectrum (b) below shows the spectrum of the annealed sample (24 K) with the satellite absorption diminished.
- Spectrum (c) and the table below show the comparison between experimental observation and theoretical predictions. The scaled theoretical predictions are in good agreement with experiment, confirming observation of the ν_5 mode.
- The ν_5 mode corresponds to an asymmetric C stretch shown in the figure below.

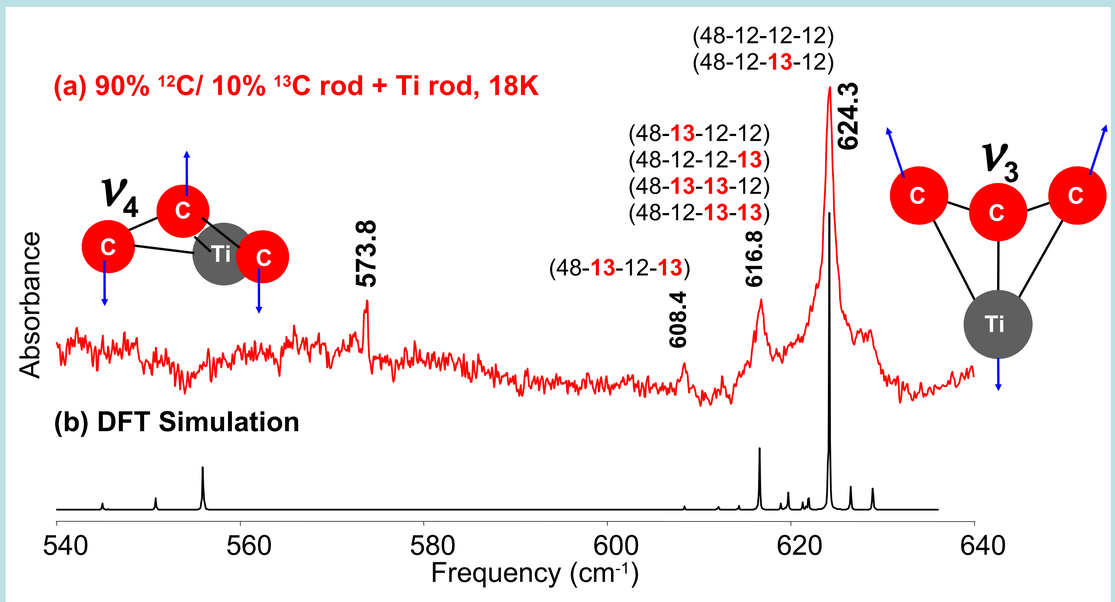


Isotopomer	Observed	B3LYP/ 6-311G(3*df*,3*pd*)	Scaled [a]	Difference
Ti-C_α-C_β-C_α	ν	ν	ν	$\Delta\nu$
48-12-12-12	1484.2	1549.4	1484.2	0.0
48-13-12-12	1473.5	1538.0	1473.3	0.2
48-12-13-12	1450.9	1513.8	1450.1	0.8
48-13-13-12	1439.9	1502.2	1439.0	0.9
48-13-12-13	1461.4	1524.9	1460.7	0.7
48-13-13-13	--	1488.6	1426.0	--

[a] Scaling factor of 1484.2/1549.4 = 0.95792 .

ν_3 fundamental

- The ν_3 fundamental is observed at 624.3 cm^{-1}. It is a symmetric Ti-C stretch (see figure below, at right).
- Comparison of the experimental and theoretical spectra shows good agreement (see table below), confirming observation of the ν_3 mode.
- The weak fundamental $\nu_4(b_1)$ due to carbon bending from the plane of the molecule may tentatively be assigned at 573.8 cm^{-1}. However, the absence of shifts precludes an unambiguous identification of this mode.



Isotopomer	Observed	B3LYP/ 6-311G(3*df*,3*pd*)	Scaled [a]	Difference
Ti-C_α-C_β-C_α	ν	ν	ν	$\Delta\nu$
48-12-12-12	624.3	696.7	624.3	0.0
48-13-12-12	616.8	688.2	616.7	0.1
48-12-13-12	overlapped	696.5	624.1	--
48-13-13-12	616.8	688.1	616.6	0.2
48-13-12-13	608.4	679.1	608.5	-0.1
48-13-13-13	--	679.0	608.4	--

[a] Scaling factor of 624.3/696.7 = 0.8961 .

Conclusions

Two fundamental vibrations and one possible candidate vibration have been detected for the C_{2v} fan-like isomer of TiC_3 trapped in solid Ar. The two identified modes are $\nu_3(a_1)$ = 624.3 cm^{-1}, and the $\nu_5(b_2)$ = 1484.2 cm^{-1}. The $\nu_4(b_1)$ vibrational mode may tentatively be assigned at 573.8 cm^{-1}. The observed frequencies are in good agreement with DFT predictions. The observed ν_3 vibration is in good agreement with the 650 ± 30 cm^{-1} observation reported in the photoelectron spectroscopy study.

Future Work

Future objectives are to characterize the structures and vibrations of additional MC_3 (M = transition metal) molecules and more complicated MC_n, n > 3 and M_mC_n molecules.

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References

X.B. Wang, C.D. Ding, and L.S. Wang, J. Phys. Chem. A **101**, 7699 (1997).
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