

N91-14915 p.5

SIMULTANEOUS INFRARED AND UV-VISIBLE ABSORPTION SPECTRA OF MATRIX-ISOLATED CARBON VAPOR

Joe Kurtz and Donald R. Huffman
Department of Physics, University of Arizona
Tucson, Arizona 85721 USA

Carbon molecules have been suggested as possible carriers of the diffuse interstellar bands. In particular, it has been proposed that the 443 nm diffuse interstellar band is due to the same molecule which gives rise to the 447 nm absorption feature in argon matrix-isolated carbon vapor. If so, then an associated C-C stretching mode should be seen in the IR. By doing spectroscopy in both the IR and UV-visible regions on the same sample, the present work provides evidence for correlating UV-visible absorption features with those found in the IR. Early data indicates no correlation between the strongest IR feature (1997 cm^{-1}) and the 447 nm band. Correlation with weaker IR features is being investigated.

INTRODUCTION

The absorption spectrum of carbon vapor trapped in a solid inert gas matrix was first reported more than 25 years ago (Weltner and Walsh, 1962, Barger and Broida, 1962). Since that time, much has become known about the molecules C_2 and C_3 , but, due to the many molecular species present in matrix-isolated carbon vapor, uncertainty remains concerning the assignment of the spectral features that seem to dominate both the UV-visible spectrum of the vapor (Krätschmer, Sorg, and Huffman, 1985) and the infrared spectrum (Thompson, DeKock and Weltner, 1971).

Carbon molecules have been suggested as possible carriers of the diffuse interstellar bands (Douglas, 1977). In particular, Krätschmer (1986) has proposed that the 443 nm diffuse interstellar band is due to the same molecule which gives rise to the 447 nm absorption feature seen in argon-isolated carbon vapor. He has further suggested that the molecule responsible is linear C_7 . Theoretical studies of small carbon molecule ground state structures (e.g. Raghavachari and Binkley, 1987) predict IR (vibrational) transitions and can be used as a basis for tentative assignments in this region of the spectrum. Unfortunately, assignment of spectral features in the UV-visible region to a particular carbon molecule based on calculations is even more tenuous. If the 447 nm feature is in fact due to a linear carbon chain such as C_7 , then an associated C-C stretching mode absorption feature should be seen in the infrared. Krätschmer's group has studied both spectral regions intensely but in separate experiments. They cannot, therefore, definitely suggest which IR features are due to this same molecule (and which are not). The purpose of this research is to correlate IR absorption features of matrix-isolated carbon vapor to those in the UV-visible by doing spectroscopy in both regions on the same sample. This research should establish correlations between the IR and UV-visible spectra, thus, for the first time, providing direct evidence for the assignment of certain UV-visible features of the long-studied carbon vapor spectrum.

EXPERIMENT

The apparatus consists of a cryostat with a cold finger extending into a vacuum chamber at the intersection of the two monochromator beams. The cryostat is mounted on the sample chamber so as to allow rotation of the cold finger to face either beam. Directly attached to the chamber are the carbon source and the vacuum UV-visible monochromator (see figure 1).

The UV-visible light source is a 75-watt high-pressure Xenon arc lamp which is mounted in a water-cooled chamber under nitrogen purge. The light is focused onto the entrance slits of the Seya-Namioka monochromator with a CaF_2 lens and passes into the monochromator vacuum chamber through a CaF_2 window. The light is dispersed with a 600 line/mm grating then passes through the exit slits directly into the sample chamber and through the sample. It is detected by a phototube whose signal is measured by a picoammeter.

The carbon source consists of an evaporation chamber in which two carbon rods are incandescently heated by passage of a large alternating current (typically 80-120 amps). The flat end of one rod is held against the tapered tip of a smaller rod by a spring under compression in its (water-cooled) mount. The evaporation chamber also has a NaCl window mounted behind the rods (away from the sample) which can be protected somewhat by a shield rotated into position during carbon deposition.

The carbon rods double as an IR light source. For this purpose the window shield is rotated out of the IR beam line and a focusing mirror is placed outside the evaporation chamber. This mirror focuses the IR beam through the sample and sample chamber window, onto the entrance slits of the IR monochromator. This monochromator was taken from a Beckman IR7 Spectrophotometer and has been fitted with a high frequency (~1KHz) light chopper and a liquid N_2 cooled HgCdTe detector. The detector output is amplified and input to a lock-in amplifier. Both the IR and UV-visible systems are operated in single beam mode.

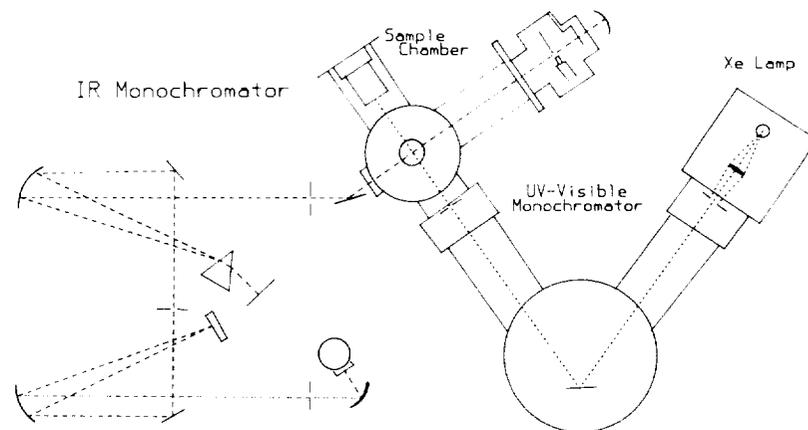


Figure 1 – Optical diagram of both monochromators.

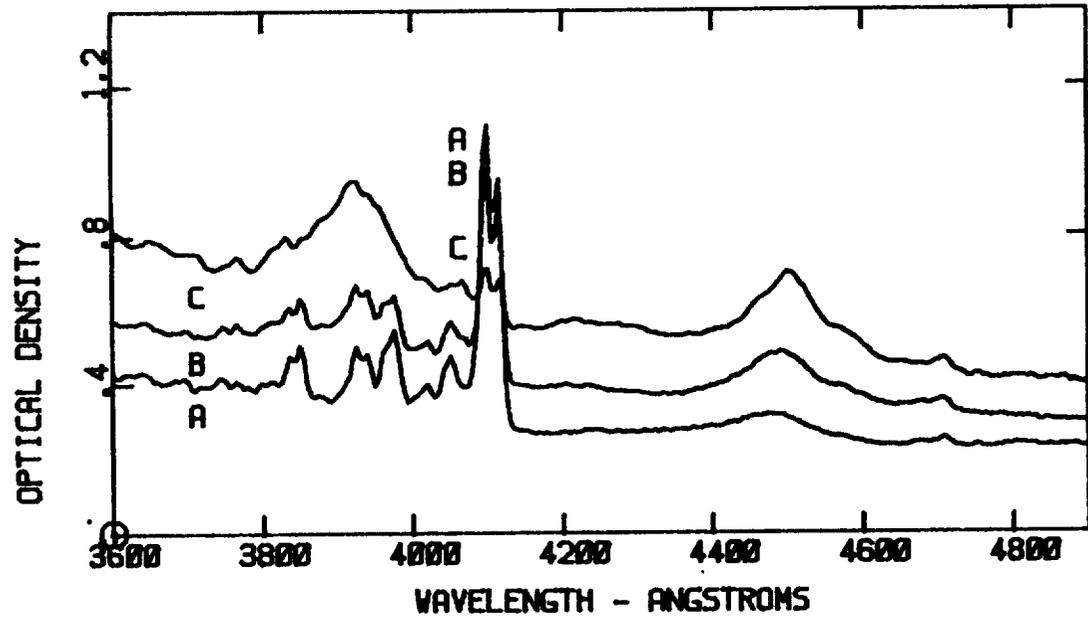
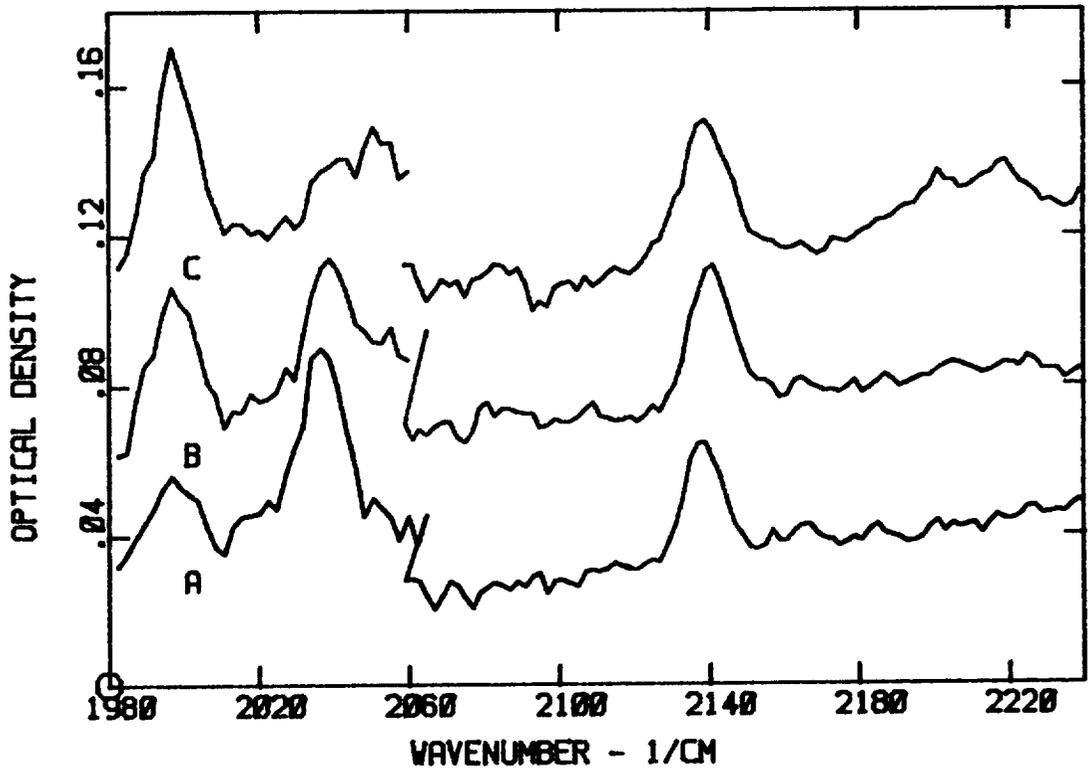


FIGURE 2 - UV-Visible (bottom) and IR (top) spectra.

The cryostat is of the continuous flow type (Oxford Instruments CF-100) wherein temperature control is accomplished by controlling the flow of helium through the cryostat as well as using a resistance heater mounted on the cryostat just above the cold finger. The temperature is measured with a carbon resistor in thermal contact with the cryostat also just above the cold finger.

Samples were prepared by successive depositions of carbon vapor, co-condensing with argon onto a low temperature (~10 K) sapphire substrate on the cryostat cold finger. Subsequent to each deposition, the sample was scanned from 1900 to 6000 Å in the UV-visible and from ~1600 to 2400 cm⁻¹ in the IR. After sufficient carbon was deposited, the sample was subjected to a series of increasingly warmer thermal annealings to promote the formation of larger molecular clusters of carbon. After each annealing, the absorption features were again scanned with the sample at 9-10 K.

Data acquisition was accomplished with a 12-bit A-to-D board and an IBM PC. The computer also controls the scanning motors of both monochromators as well as the phototube voltage and a programmable gain op-amp IC which is in-line to the A-to-D input. Software generated by one of the authors (JK) was used to run the monochromators, acquire data and generate the spectral output.

EARLY DATA AND RESULTS

Figure 2 shows portions of spectra from the same experimental run. Curves labeled A, B and C are spectra of the sample after deposition, after two annealing periods and after four annealing periods, respectively. Each annealing period was for about ten minutes. The first was at 20 K with the temperature incremented by about 5 K for each subsequent annealing. Spectra were taken after each annealing, but only two are shown for clarity.

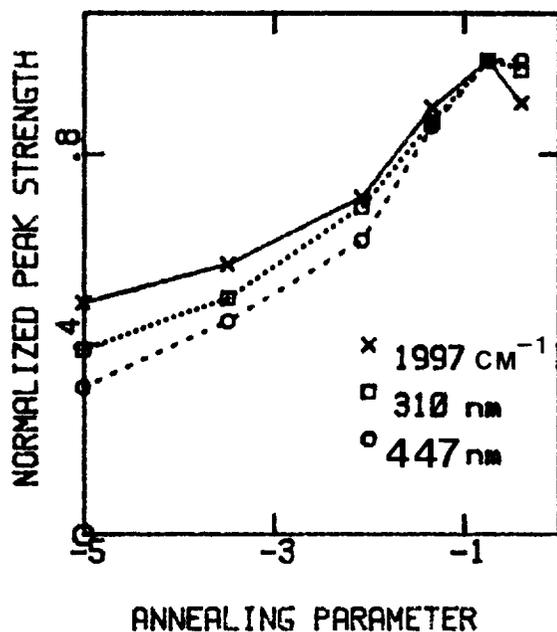


FIGURE 3

Excellent agreement has been observed among the many features found in the UV-visible with the same spectral features found by Krätschmer's group. As annealing proceeds, the known C₃ band at about 410 nm (Figure 2, bottom graph) decreases as the 447 nm band and other bands increase, suggesting that these bands are due to larger clusters of carbon atoms. The infrared spectrum shown in figure 2 (top) also shows a known C₃ feature at about 2039 cm⁻¹ which can be seen decreasing as the strong 1997 cm⁻¹ feature increases. At 2139 cm⁻¹ a large CO feature is present with an unresolved feature at 2128 cm⁻¹. Features growing at 2054, 2200 and 2220 are also shown. Many more IR features are present, but not shown here.

By following the evolution of absorption features in the two regions, correlations can be found. Uncertainties limit the conclusiveness of the possible correlations, particularly because of the low absorption above baseline of the infrared features and the limited IR resolution. With perhaps more certainty, some correlations can be ruled out. Figure 3 shows normalized peak strength above baseline versus an annealing parameter (time and temperature dependent) for two UV-visible features (at 310 nm and 447 nm) and the strongest infrared feature (1997 cm⁻¹).

The 1997 cm^{-1} feature is adequately above the noise even at deposition to conclude that it does not correlate well to the 447 nm feature which is poorly developed at deposition. The 310 nm band seems to be better correlated to this IR feature, although it too is relatively weak in the early stages of annealing. Weaker IR features are being explored, but with the data so far collected, they cannot yet be established as companions of the 447 nm feature.

REFERENCES

- Barger, R.L. and Broida, H.P.: 1962, *J. Chem. Phys.* **37**, 1152.
- Douglas, A.E.: 1977, *Nature* **269**, 130.
- Krätschmer, W.: 1986, *Astrophysics and Space Sciences* **128**, 93.
- Krätschmer, W., Sorg, N., and Huffman, D.H.: 1985, *Surface Sci.* **156**, 814.
- Raghavachari, K. and Binkley, J.S.: 1987, *J. Chem. Phys.* **87**, 2191
- Thompson, K.R., DeKock, R.L., and Weltner, W.: 1971, *J. Am. Chem. Soc.* **93**, 4688.
- Weltner, W. and Walsh, P.N.: 1962, *J. Chem. Phys.* **37**, 1153.

