The Diffuse Interstellar Bands
Proceedings IAU Symposium No. 297, 2013
J. Cami & N. L. J. Cox, eds.

doi:10.1017/S1743921313016013

Developments of Optical Spectrometers as Approaches to Diffuse Interstellar Bands

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Abstract. A discharge-emission spectrometer and a cavity ringdown spectrometer have been developed to aid in the solution to the diffuse interstellar band (DIB) problem. A hollow cathode was used to generate molecular ions in a discharge because it has been suggested that molecular ions are probable DIB candidates. The discharge was produced by a pulsed voltage of 1300 − 1500 V. A wide wavelength range of optical emission from the discharge was examined by a HORIBA Jobin Yvon iHR320 monochromator. The dispersed discharge emission was detected by a photomultiplier and was recorded via a lock-in amplifier. The $^2B_{3u} - X^2B_{2g}$ electronic transition of the butatriene cation $H_2CCCCH_2^+$ was observed in the discharge emission of 2-butyne H_3CCCCH_3. The frequency of the electronic transition was measured to be 20381 cm^{-1}, and a comparison study was made with known DIB spectra.

The resolution of the discharge-emission spectrometer is insufficient to make precise comparisons between laboratory frequencies and astronomically observed DIB spectra. We therefore developed the cavity ringdown spectrometer using the same hollow cathode. The high sensitivity of this spectrometer was confirmed by the observation of the forbidden band of O_2.

Keywords. methods: laboratory, techniques, astrochemistry, plasmas

1. Introduction

Diffuse interstellar bands (DIBs) still remain the longest standing unsolved problem in spectroscopy and astrochemistry, although several hundreds of DIBs have been already detected. One of the best approaches to identifying the carrier material of DIBs is the generation and measurement of DIB candidate molecules in the laboratory to compare their absorption spectra with astronomically observed DIB spectra.

Molecular ions, especially cations, in the gas phase are potential DIB candidate molecules (Jochnowitz & Maier 2008). The electronic transition of the cations of polyaromatic hydrocarbons and unsaturated carbon chain molecules result in optical absorption. However, because cations are unstable, their electronic transitions are difficult to observe using a laboratory spectrometer system. To solve this difficulty, we have developed a glow-discharge cell using a hollow cathode in which cations can be effectively produced as a high-density plasma by the hollow-cathode effect. Hollow-cathode glow discharges of molecular gas can produce many types of cations, including those previously unpredicted. We have also developed a discharge-emission spectrometer and a cavity ringdown spectrometer to detect the spectra of cations in the laboratory.

2. Discharge-Emission Spectrometer

A hollow cathode with an internal diameter of 21 mm and length of 20 mm installed at 80 mm from an anode was used to generate cations in a glow discharge. The discharge cell was made from a Pyrex glass tube having a length of 30 cm and an internal

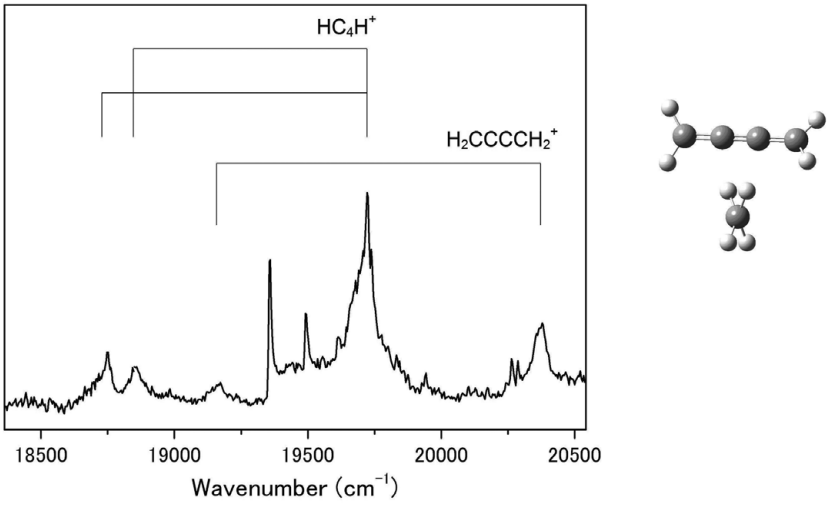

Figure 1. The observed spectrum of the 1,2,3-butatriene cation $H_2CCCCH_2^+$ with the discharge-emission spectrometer.

diameter of 3.3 cm. The hollow-cathode glow discharge was produced by a pulsed voltage of 1300 − 1500 V having a pulse width of 1 ms at 400 Hz. The pulsed voltage was produced by a combination of a fast high voltage transistor switch (BEHLKE HTS 31) and a custom-built high-voltage power supply. The typical voltage and current between the electrodes were 500 − 800 V and 30 − 50 mA, respectively, with a ballast resistance of 20 kΩ and a small hydrocarbon molecular gas held at a pressure of 0.2 torr without carrier gases for molecular discharge. A monochromator (HORIBA Jobin Yvon iHR320), having a wide spectral range of 200 − 800 nm and which used three gratings having groove densities of 1200 − 1800 gr/mm, was used to examine discharge spectra. These gratings provided a FWHM resolution of ∼10 cm^{-1} by a slit width of 0.1 mm. The discharge emission from the hollow cathode was focused on the inlet of the monochromator. The dispersed discharge emission was detected by a photomultiplier (Hamamatsu R928), to which a voltage of −650 V was applied, and the signal was measured by a digital multimeter (Sanwa PC5000) via a lock-in amplifier (Femto LIA-MV-200-L). The signal was transferred from the multimeter to a personal computer. The movement of the monochromator and the acquisition of the signal were managed by a graphical programming language LabVIEW application. Observed spectra were calibrated to those of argon atomic lines.

We are the first to detect the 1,2,3-butatriene cation $H_2CCCCH_2^+$ in the discharge of 2-butyne H_3CCCCH_3 (Fig. 1, Araki *et al.* 2013). The band observed at 20381 cm^{-1} (4905Å) in the discharge with the discharge-emission spectrometer was assigned to the $^2B_{3u}-X^2B_{2g}$ transition of $H_2CCCCH_2^+$ on the basis of the sample gas dependences and the reported photoelectron spectrum (Brogli *et al.* 1974). The observed vibrational band at 19174 cm^{-1} was assigned to the torsional band. However, upon comparison of the band with known DIBs, no related DIBs were found at present (Jenniskens & Desert 1994, Bondar 2012).

3. Cavity Ringdown Spectrometer

The cavity ringdown (CRD) spectrometer consists of a tunable pulse laser system, an optical cavity and a discharge device (Fig. 2, Left, Linnartz *et al.* 1998, Motylewski

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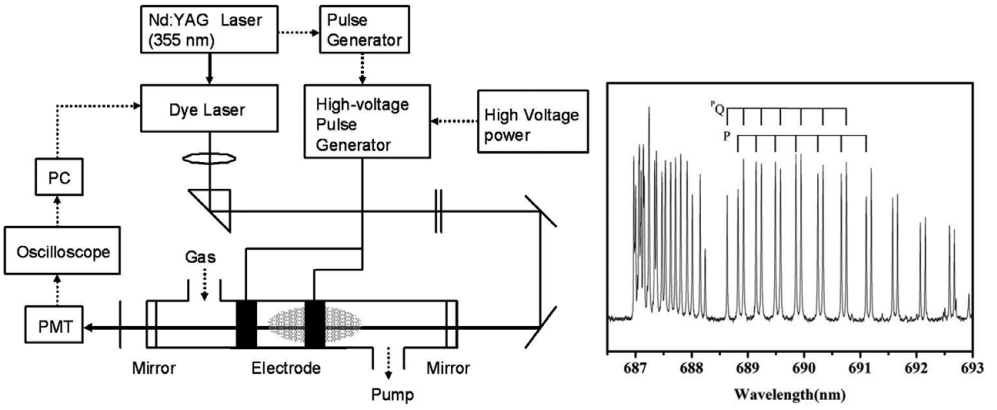

Figure 2. Conceptual diagram of the cavity ringdown spectrometer and the observed $b^1\Sigma_g - X^3\Sigma_g$ (1-0) band of O_2.

& Linnartz 1999). The tunable pulse laser beam was taken from a dye laser (ND6000, Continuum) pumped by a Nd:YAG laser (355 nm, Surelit). The optical cavity was constructed with two high reflectivity mirrors ($R > 99.995\%$, Los Gates Research). The discharge cell was located in a vacuum chamber that was evacuated by a rotary pump. The hollow-cathode glow discharge was produced by a pulsed voltage of $1300 - 1500$ V with a pulse width of 1 ms. Typically, sample gas without buffer gas was used in the discharge system. The obtained discharge pulse was synchronized with the laser pulse by a custom-build pulse generator. The whole experiment runs at 10 Hz. The ringdown signal was displayed on an oscilloscope. The signal was transferred to a data acquisition system including a ringdown calculation function that was developed with LabVIEW.

Test observations of the CRD spectrometer using Ar, Ar^+, C_2, and O_2 as the discharge gas were successfully achieved. The production of cations was tested by using the electronic transitions of Ar^+ compared with Ar. The cation:neutral ratio of Ar in the hollow-cathode glow discharge was found to be $Ar^+/Ar = 0.1 - 0.01$. The rotational temperature in the discharge was measured to be 400K by means of observation of the Swan band of C_2. The very weak forbidden $b^1\Sigma_g - X^3\Sigma_g$ transition of O_2 was observed in the S/N = 300 (Fig. 2, Right), which suggests high sensitivity and high resolution of this spectrometer system.

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