

## The infrared spectrum of CN in its ground electronic state

(Heyrovský Institute<sup>1</sup>, 岡山大理<sup>2</sup>) ○S. Civiš<sup>1</sup>, V. Horká<sup>1</sup>, V. Špirko<sup>1</sup>, 川口建太郎<sup>2</sup>

**【Introduction】** The CN free radical is observed in interstellar molecular clouds and atmospheres of stars, planets and comets. It is also significant in numerous laboratory processes at high temperatures (flames, chemical reactions, discharges) where it is often formed from trace amounts of carbon and nitrogen. This is a very strong absorber / emitter of radiation and its spectra, extending from the vacuum UV far into the infrared without significant gaps, provide a very useful tool for its detection and monitoring. A vast portion of the available spectral data arises from the  $A^2\Pi \rightarrow X^2\Sigma^+$  and  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  electronic transitions [1] and the infrared transitions in the  $X^2\Sigma^+$  ground electronic state [2] (see Fig.1). From the point of view of the vibrational excitation, the most important information is obtained from vibronic data involving vibrational levels up to  $v = 18$ . Such high vibrational excitation corresponds to temperatures well above 10 000 K thus indicating the potential use of CN in high temperature monitoring and the possibility of experimental determination of the molecular potential energy function. Coverage of the rotational excitation by the available data, however, is not as complete. The vibronic data [1] exhibit gaps for some vibrational states and the vibrational data [2] include vibrational levels only up to  $v = 4$ .

The aim of this study is to improve the coverage of the ro-vibrational data for CN and to determine its “experimental” potential energy function over a wide range of vibrational displacements. For this purpose, we have concentrated primarily on measuring the wave numbers of many lines as possible in the system of the ( $v' \rightarrow v''$ ) transitions which is covered by our spectral facilities. The “global” potential energy function was constructed by “morphing” the *ab initio* potential of Polák and Fišer [3] within the framework of the reduced potential curve method of Jenč [4, 5].

**【Experimental】** The spectra were recorded from the emission of the positive column of a glow discharge plasma with a Bruker 120 HR Fourier Transform high resolution interferometer equipped with an InSb detector. The discharge glass tube was 20 cm long with an inner diameter of 12 mm. The DC discharge was maintained by high voltage applied to two stainless steel electrodes. The smaller anode was oriented closer to the iris of the spectrometer. To reduce the electric and sputtering noise signal, the (cylindrical glass-metal sheet) cathode was chosen to be much larger than the anode. The voltage drop across the discharge was 700 V and the discharge current was 50 mA.

The radiation from the discharge plasma was focused by a  $\text{CaF}_2$  lens onto the iris of the spectrometer. The plasma made from a mixture of cyanogens  $(\text{CN})_2$  and helium was cooled by flowing water or liquid nitrogen in the outer jacket of the cell. The best conditions for generating the CN radical in its  $X^2\Sigma^+$  ground state were found to be  $P(\text{He}) = 5$  Torr and  $P(\text{CN})_2 = 0.01$  Torr (all pressures measured with the cell at room temperature).

The recording spectral range was about 1800-4000  $\text{cm}^{-1}$ , at an unapodized resolution of 0.027  $\text{cm}^{-1}$ . The recording number of scans was about 50 to obtain a reasonable signal-to-noise ratio. An observed spectrum is shown in Fig. 1, where the A-X electronic transitions are clearly seen in addition to the vibrational bands. Lines of CO and  $\text{CO}_2$  present in the spectra as impurities were used for calibration of the line positions. The post zero filled spectrum and accumulated line profiles were analyzed using the Bruker OPUS software.

**【Analysis】** The point-wise calculated *ab initio* energies [3] were smoothed (by a quantitative least-squares fitting) using the following potential energy function

$$U(r) = \sum_p F_p \left\{ 1 - e^{-a(r-r_p) - b(r-r_p)^2 - c(r-r_p)^3} \right\}^p + C_3 / r^3 + U_0, \quad (1)$$

where  $r$  is the internuclear distance and  $a$ ,  $b$ ,  $c$ ,  $F_p$ ,  $r_p$ ,  $C_3$  and  $U_0$  are the fitting parameters. The corresponding theoretical ro-vibrational energies were found as eigenvalues of the radial Hamiltonian (the hyperfine interactions were disregarded)

$$H^{rv} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + U(r) + \frac{\hbar^2}{2\mu r^2} N(N+1), \quad (2)$$

where  $\hbar$  is the Planck constant,  $\mu$  is the reduced mass and  $N$  is the rotational quantum number. The reduced potential curve scheme used in the present paper has the following (generalized) form [4, 5].

$$u = \frac{U}{D_e}, \quad (3)$$

$$\rho = \frac{r - \{1 - \alpha \exp[-\beta(1 + \gamma r) / \rho_{ij}]\} \rho_{ij}}{r_e - \{1 - \alpha \exp[-\beta(1 + \gamma r) / \rho_{ij}]\} \rho_{ij}}, \quad (4)$$

$$\rho_{ij} = \frac{r_e - (\kappa D_e / k_e)^{1/2}}{\{1 - \alpha \exp[-\beta(1 + \gamma r) / \rho_{ij}]\} \rho_{ij}}, \quad \kappa = 3.96, \quad (5)$$

where  $\rho$ ,  $u$  and  $U$  are the reduced internuclear distance, the reduced energy and the genuine potential, respectively;  $D_e$ ,  $r_e$ , and  $k_e$  are the depth of the minimum of potential curve, the equilibrium internuclear distance, and the harmonic force constant, respectively;  $\kappa$  is the universal “reduced” force constant;  $\alpha$ , and  $\beta$  are “correction” parameters (in the standard RPC formula,  $\alpha = 1$  and  $\beta = 1$ ).

**[Summary]**  $^{12}\text{C}^{14}\text{N}$  vibration-rotation bands for the sequences  $v = (1-0)$  through  $(9-8)$  were observed in the spectral region  $1800-2200 \text{ cm}^{-1}$ . Of the 362 lines observed, the wave numbers of 237 lines were least-squares fitted using the Dunham expansion coefficients with a root-mean-square deviation of  $0.00091 \text{ cm}^{-1}$ . Together with the most accurate data from the literature, the data were fitted in the framework of the Reduced Potential Curve (RPC) method. The global potential energy function resulting from this fit provides a fairly quantitative description of the experimental data, at least up to  $30000 \text{ cm}^{-1}$ . In addition to global fitting, the RPC approach was also used for fully quantitative fitting of the data pertaining to the lowest three vibrational states. The effective potential energy curves obtained in this way allow for very accurate predictions of highly excited rotational states.

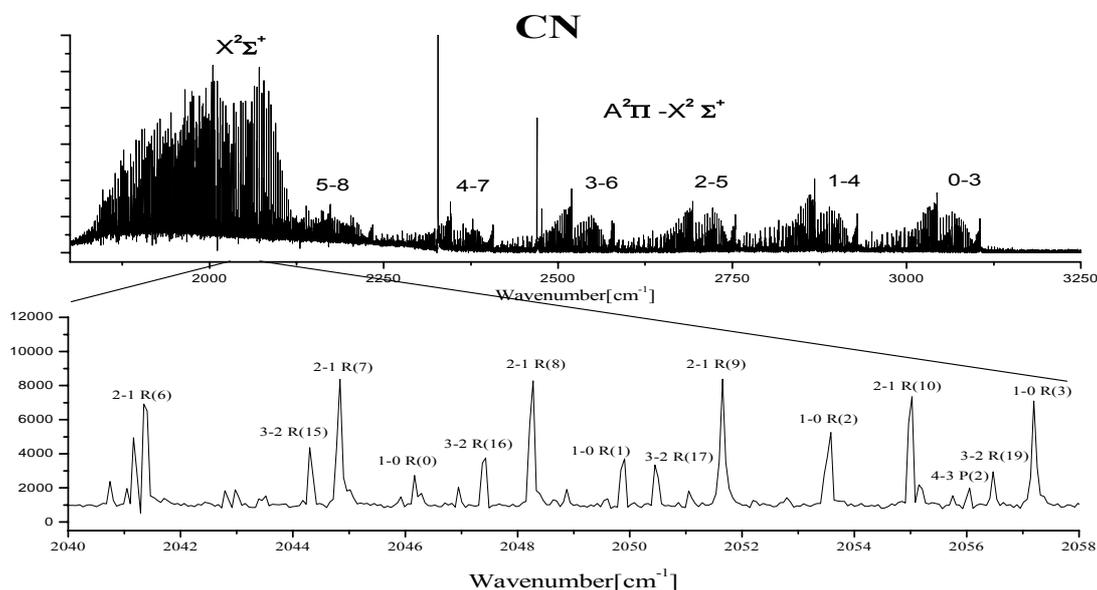


Fig.1 Observed emission spectrum of CN

#### References

- [1] Ito H., Kazama A., Kuchitsu K.: *J. Mol. Struct.* **1994**, 324, 29.
- [2] Davis S. P., Adams M. C., Rao M. L. P.: *J. Opt. Soc. Am.* **1991**, B8, 198
- [3] Polák R., Fišer J.: *Coll. Czech. Chem. Commun.* **2003**, 324, 324
- [4] Jenč F.: *Int. Rev. Phys. Chem.* **1996**, 15, 467
- [5] Bludský O., Juřek M., Širko V., Brandt B. A., Jenč F.: *J. Mol. Spectrosc.* **1995**, 169, 555