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## Raman Effect of Sodium Cyanide

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## RAMAN EFFECT OF SODIUM CYANIDE

GEO. GLOCKLER AND H. T. BAKER

In another study we wished to use the Raman line of sodium cyanide solution as a reference spectrum. We find that potassium cyanide solutions but not sodium cyanide have been studied by Pal and Sen Gupta (1930). It is well known that electrolytes which are strong salts and hence highly ionized in solution give Raman lines only of their ions in case the latter are complex. Hence only the Raman spectrum of the cyanide ion is to be expected from any cyanide solution independent of the positive ion. Only one frequency should be observed due to the vibration of the carbon and nitrogen atoms relative to one another. However Pal and Sen Gupta reported two frequencies: 838 and 2080  $\text{cm}^{-1}$ . From studies on other cyanides such as hydrogen cyanide (Hibben, 1939) the higher value evidently belongs to the carbon-nitrogen vibration in the cyanide ion. The lower frequency must therefore be spurious in some way. The first idea that always comes to mind at this juncture is the possibility that the given frequency has been deduced by the use of a wrong exciting line. However we convinced ourselves speedily that this error could not have been made. The next possibility is the search for an impurity which might give rise to a low vibration (838  $\text{cm}^{-1}$ ). It was indeed found that potassium cyanate has a frequency of just this value and it seems clear that this line is due to the presence of a small amount of cyanate in the cyanide used. This impurity could easily arise by gradual oxidation of the initial cyanide by the oxygen of the air. In order to be certain of our contention we measured the Raman spectrum of sodium cyanide solutions.

*Experimental Results.* An approximately saturated solution of sodium cyanide (C.P.) in water was prepared by dissolving 465 gms. of the salt per liter of solution in accordance with the solubility determination of Kireev and Vagranskaya (1935). The solution was actually used at 25°C and hence no difficulty was encountered because of precipitation. The solution gave a bright Tyndall beam of greenish blue color. It also gave a decided background on the photographic plate in the region 4358 to 4916 angstroms. However filtering several times through animal charcoal and Fuller's earth cut down the intensity of the Tyndall beam considerably and resulted in very little background in the

above mentioned region. It was now possible to obtain a clear, sharp Raman line of  $2086.7 \text{ cm}^{-1}$  (Table I). No other line was found on any of our plates.

*The Force Constant.* Since the frequency of the CN-Bond appears now to be known it seemed of interest to calculate the force constant ( $k$ ):

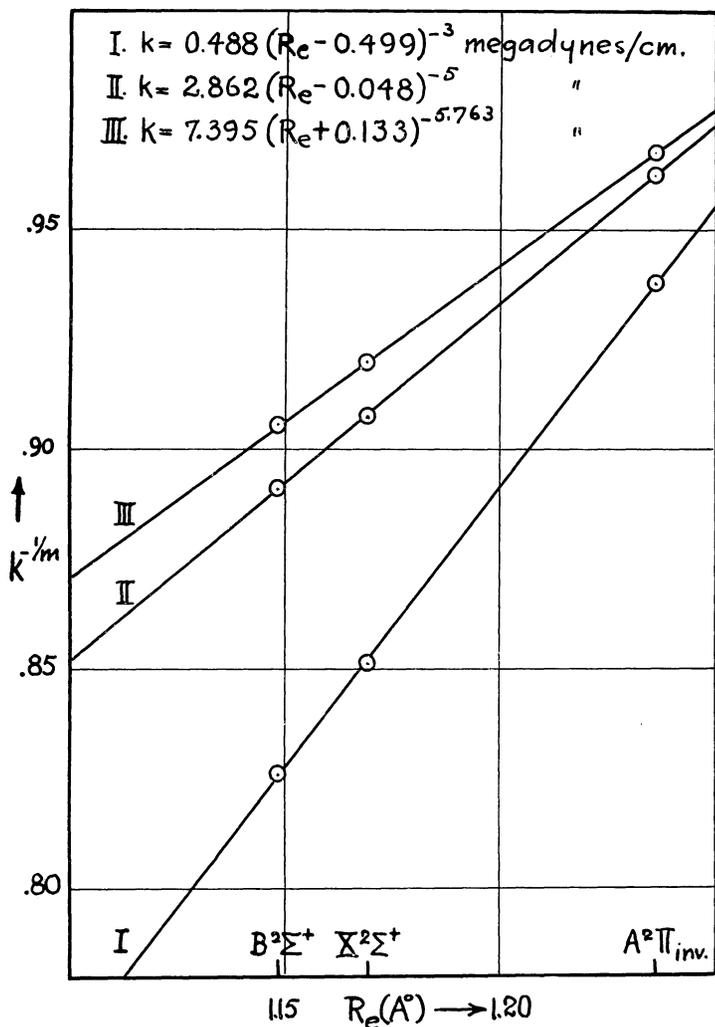
$$k = 0.05863 \mu \omega^2 = 1.65 \times 10^6 \text{ dynes/cm} \quad (1)$$

where  $\mu$  is the reduced mass of the cyanide radical on the atomic weight scale ( $C = 12$ ,  $N = 14$ ) and  $\omega$  is the frequency in wave numbers. This value is for the cyanide ion in solution. For comparison we have calculated the force constant of the CN-group in various spectroscopic states taken from Jevons (1932) and of several other compounds containing the CN-group. The frequencies were taken from Hibben (1939) and the results are given in Table II. An application of Badger's (1934, 1935) rule which is an empirical relation between the force constant and the equilibrium inter atomic distance ( $R_e$ ) is shown in Figure I. The three spectroscopic states ( $B^2\Sigma^+$ ,  $X^2\Sigma^+$  and  $A^2\Pi_{inv}$ ) are used to determine the straight line connecting  $k^{-1/3}$  and  $R_e$ . If the same relation holds for the CN-group in other molecules, the respective interatomic distance can be obtained graphically or from the equation

$$k = 0.488 (R_e - 0.499)^{-3} \text{ megadynes/cm} \quad (2)$$

The values of  $R_e$  are shown in the fourth column of Table II. The attempt to compare these distances with other data is rather unsuccessful. Electron diffraction experiments cited by Brockway (1936) are not extensive enough and not of sufficient high accuracy to permit a decision to be made. In cyanogen and methyl cyanide the empirical rule values are lower than the electron diffraction values. It is to be hoped that the latter method can be developed to a higher degree of precision so that the present application may be tested.

*Potential energy curve.* In a further attempt to make use of the vibration frequency it is always interesting to construct a potential energy curve, because the second derivative of the potential energy in respect to distance of separation evaluated at the equilibrium distance is the force constant. The most satisfactory curve of this kind is the Morse (1929) curve. It is entirely empirical but the Schroedinger's equation can be solved (Hellmann, 1937). Lately Born and Mayer (1931) have employed a potential energy curve for crystals which has a power term for attraction and an exponential repulsive term. This mathematical structure is more sat-



### Force Constant of Cyanide Radical and internuclear distance

isfactory on the basis of modern considerations and we have adopted this form of expression for the present case:

$$U(R)/D = 1 - 2(R_e/R)^m + \exp(-B(R - R_e)) \quad (3)$$

$U(R)$  is the potential energy of the system when the atoms are a distance  $R$  apart. One of the atoms is located at the origin.  $D$  is the heat of dissociation.  $R_e$  is the equilibrium distance,  $m$  is a numerical exponent and  $B$  is a constant. The function is unsatis-

factory near R equals zero, where it approaches a negative infinite value. However this region is of no importance in our considerations. Differentiation of (3) yields

$$dU/dR = 2DR_e^m \cdot m R_e^{m-1} \cdot R_e^{-2m} - DB \exp(-2B(R-R_e)) \quad (4)$$

This quantity (the force between C and N) must be zero when  $R = R_e$ :

$$2Dm/R_e - DB; B = 2m/R_e \quad (5)$$

The second derivative evaluated at  $R = R_e$  yields the force constant k:

$$k = 2Dm(m - 1)/R_e^2 \quad (6)$$

The value of the exponent m can be obtained from the spectroscopic data of Jevons (1932) who also gives the heat of dissociation. The values of m so calculated are given in Table II (column 7) and their average is

$$m = 3.763 \pm 0.121 (\pm 3.2\%) \quad (7)$$

If we assume that this value is constant for the CN-group in combination with other atoms and radicals we can calculate the heat of dissociation (D) from the force constant (k) and the equilibrium distance ( $R_e$ ):

$$D = 3.0 k R_e^2 \quad (8)$$

D is given in electron-volt, k is megadynes per cm and  $R_e$  is expressed in angstroms. The calculated values are given in Table II (column 8). Sutherland (1938) studied a potential energy curve containing two inverse power terms. As stated above the present case seems more satisfactory on the basis of modern concepts (Born and Mayer, 1931). Expression (3) can be rewritten

$$V = U(R) - D = -aR^m + b \exp(-R/c) \quad (10)$$

where a, b and c are constants. If a is nearly the same for the

TABLE I

Raman Line of Cyanide Ion  
(4358A° Hg excitation)

Plate	cm-1
I	2089
II	2084
III	2083
IV	2092
V	2087
VI	2085

Average: 2086.7 ± 2.7 cm-1

TABLE II  
Equilibrium Distance and Heat of Dissociation  
of the CN-group

Compound	$\omega$ cm <sup>-1</sup>	k x10 <sup>-6</sup>	Equilibrium Distance =			m	D(e.v.)	
			R <sub>e</sub> (A°)				calc.	expt.
			(1)	(2)	(3)			
(CN) <sub>2</sub>	2334	2.064	1.117	1.117	1.16±.02	3.763	7.73	---
CH <sub>3</sub> CN	2250	1.918	1.132	1.132	1.16±.02	3.763	7.36	---
CN (B <sup>2</sup> Σ <sup>+</sup> )	2164.15	(1.774)	(1.148)	(1.148)	---	3.944	7.01	6.30
HCN (liq)	2096	1.664	1.163	1.163	---	3.763	6.75	---
HCN (gas)	2089	1.653	1.164	1.165	---	3.763	6.72	---
NaCN (soln)	2086.7	1.650	1.165	1.165	---	3.763	6.71	---
NaCN (cryst)	2085	1.647	1.165	1.166	---	3.763	6.71	---
KCN (soln)	2080	1.639	1.166	1.167	---	3.763	6.69	---
CN (X <sup>2</sup> Σ <sup>+</sup> )	2068.79	(1.621)	(1.169)	(1.169)	---	3.666	6.65	7.09
CN (A <sup>2</sup> π <sub>inv</sub> )	1788.66	(1.212)	(1.236)	(1.236)	---	3.679	5.54	5.74

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(1) from empirical rule (Badger).  
(3) from electron diffraction experiment.

(2) from empirical inverse fifth power rule.

CN-group in its various states,  $k$  can be written

$$k = \text{const. } R_e^{-(m+2)} \quad (11)$$

with  $m = 3$  we find that

$$k = 2.86 \times 10^6 (R_e - 0.048)^{-5} \quad (12)$$

Calculated values of  $R_e$  are shown in Table II (column 5). The basic values of the spectroscopic states ( $B^2\Sigma^+$ ,  $X^2\Sigma^+$  and  $A^2\Pi_{inv}$ ) give a straight line as is the case with Badger's rule. However on purely mathematical grounds an inverse fifth power relation should yield nearly a straight line if an inverse third one does. Hence neither is to be preferred. An inverse 5.763 power relation gives a somewhat better straight line than the other values of  $m$  (3 or 5).

It is evident that these studies if carried out with greater precision will permit the determination of atomic radii and heats of dissociation of bonds in molecules.

*Summary.* The fundamental frequency of the CN-group is  $2086.7 \text{ cm}^{-1}$ . A lower frequency of  $838 \text{ cm}^{-1}$  obtained by earlier investigation is due to the cyanate ion present as an impurity. The force constant of the cyanide ion is 1.65. megadynes per cm. A comparison is made of the force constants of the CN-group in various molecules and spectroscopic states and the internuclear distance. Badger's rule holds. A potential function is discussed and the exponent of the repulsive term is found to be  $3.763 \pm 0.121$  from band spectrum data. The heat of dissociation of the CN-group is calculated from the force constants, the equilibrium distance obtained from the inverse third power rule and the average value of the repulsive exponent.

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