# The Raman Spectrum of Cyanuric Acid

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## Introduction

From the experimental results of the ultraviolet absorption spectra, E. Agallidis and his coworkers as well as I. M. Klotz and Themis Askounis have concluded that enol-and keto-formal cyanuric acids coexist in aqueous solution in the tautomeric relation.(1),(2) In the present work, the author tried to ascertain this from the view-point of Raman spectrum, and computed further approximate force constants for both forms by simple calculations.

## Experimental

For photographing Raman spectra a powerfully light-gathering spectrograph constructed by us was used. It had two dense flint prisms (height 4.5 cm, side length 6 cm), a collimator lens (diameter 9 cm., focus 45 cm.) and a camera lens (diameter 8 cm., focus 21 cm.). Two glass mercury lamps were used as the light source, placed on both sides of the wood-type Raman tube. The exposure time, on "Oriental" Hyper Panchromatic plates, ranged from 10 to 100 hours.

A sample of pure cyanuric acid, recrystallized from water three times, was dissolved in a hydrogen chloride acidic and a caustic soda alkaline solution. As the concentration of the aqueous solution at room temparature could not be made greater than about 10 %, although water seems to be the best solvent for the acid, a rather long exposure time was needed to record measurable Raman lines. During the exposure hot water was circulated continually through the outer jacket of the wood tube in order to prevent the precipitation of crystal.

Table 1 lists wave number shifts measured in the Raman spectra of both the acidic and alkaline solutions, with indications of their relative intensities and exciting mercury lines.

## Discussion

As shown in Table 1, there are some Raman lines which have nearly coinciding wave number shifts, but with changing relative intensities observed in the two solutions. For example, 708 cm.$^{-1}$ measured for the alkaline solution and 715 cm.$^{-1}$ measured for the acidic solution, giving the same Raman shift within experimental error, shows a much greater intensity in the alkaline solution. Other such examples are found in the pairs of 331 and 329, 432 and 425, and 1410 and 1421 cm.$^{-1}$.

Table 1

Observed Raman lines of cyanuric acid in the acidic and alkaline solutions

| Alkaline solution | | | Acidic solution | | |
|---|---|---|---|---|---|
| Wave number shift (cm.$^{-1}$) | Exciting mercury line | Relative intensity | Wave number shift (cm.$^{-1}$) | Fxciting mercury line | Relative intensity |
| 331 | e | 3 | 329 | e | 1 |
| 432 | e | 3 | 425 | e, k | 1 |
| 456 | e, k, i | 1 | | | |
| 572 | e, k, i | 2 | | | |
| 708 | e, —e, k | 8 | 715 | e, k | 3 |
| | | | 816 | e, k | 3 |
| 853 | e | 3 | 853 | e, k, i | 6 |
| 923 | e, k | 3 | 921 | e | 4 |
| 1090 | k, i | 2 | | | |
| | | | 1371 | e, k, i | 2 |
| 1410 | k, i | 4 | 1421 | e, k, i | 2 |
| | | | 1636 | k, i | 5 |
| | | | 3446 | e, k, i | 6 |
| | | | 3488 | e, k | 4 |

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(1) E. Agallidis, H. Fromherz and A. Hartmann, *Ber.*, **71**, 1391 (1938).

(2) I. M. Klotz and Themis. Askounis, *J. Am. Chem. Soc.*, **69**, 801 (1947).

On the other hand, there are some pairs of lines whose intensities are in the reverse ratio, that is, strong in the acidic and weak in the alkaline solution. The pairs 853 and 853, and 923 and 921 cm.$^{-1}$ belong to this type.

Such a change of relative intensities of the corresponding Raman lines can be readily understood by assuming that tha enol-and keto-formal cyanuric acids coexist in aqueous solution and that the equilibrium between them changes with the $p$H of the solution. This assumption is in agreement with and supports the result of ultra-violet absorption.(1),(2)

In caustic soda alkaline solution, cyanuric acid exists more stably in the form of cyanuric acid ion represented by formula (1) in Fig. 1, while in acidic solution the keto form represented by (11) is more stabilized. Then the Raman lines which are stronger in the alkaline solution must be due to (1), and those stronger in the acidic solution to (11). Accordingly the shifts 331, 432, 708 and 1410 cm.$^{-1}$ are attributed to (1), and those of 853, 921, 1636, 3446 and 3488 cm.$^{-1}$ to (11).

Let us consider first the frequencies of totally symmetric vibrations of the cyanuric acid ion of form (1). X-ray diffraction studies show that the symmetry in cyanuric acid crystal is $D_{3h}$.(3)

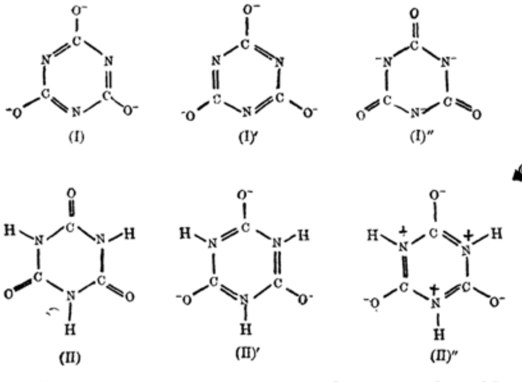

Fig. 1.—Resonance structures for cyanuric acid of enol-and keto-forms.

Assuming the same symmetry also for the ion (1), there are in all three totally-symmetric vibrations. As totally-symmetric vibrations generally appear strongly in the Raman effect,(4) it is reasonable to consider that among the four strong lines attributed by us to (1) (either one of 331 or 432, 708 and 1410 cm.$^{-1}$) the first one is probably the totally-symmetric deformation vibration of the six-membered ring, the second the totally-symmetric breathing vibration of the whole ion, and the last the totally-symmetric stretching vibration of the carbon and oxygen atoms.

On a crude assumption that cyanuric acid ion resonates only between the two Kekulè-like structures (1) and (1)′ in Fig. 1, the totally-symmetric vibration frequencies were calculated using the valence-force-field model.(4)

For the force constants the following values were used:

$k$ (C—O) $= 5.00 \times 10^5$ dyne/cm.,(5)
$k$ (C—N) $= 7.6 \times 10^5$ dyne/cm.,(5)
$\delta$ ($\angle$NCN) $= 0.23 \times 10^5$ dyne/cm.,(6)
$\delta$ ($\angle$CNC) $= 0.32 \times 10^5$ dyne/cm.,(6)

where $k$ and $\delta$ refer to stretching and bending vibrations respectively. The three totally-symmetric vibration frequencies and the corresponding vibrational types are

481 cm.$^{-1}$: deformation vibration,
904 cm.$^{-1}$: breathing vibration,
and 1288 cm.$^{-1}$: stretching vibration of the c-o bonds.

These calculated frequencies, however, do not agree well with the Raman frequencies observed above, meaning that the force constants used are not suitable. An attempt was made then to derive more reasonable force constants by substituting the obsered Raman frequencies into the final equations of the frequency calculation and to interpret their meaning. For this purpose 708 and 1410 cm$^{-1}$ were taken as the two totally-symmetric non-deformation vibrations because of their prominent intensities. For the remaining totally-symmetric frequency we may choose either 331 or 431 cm.$^{-1}$.

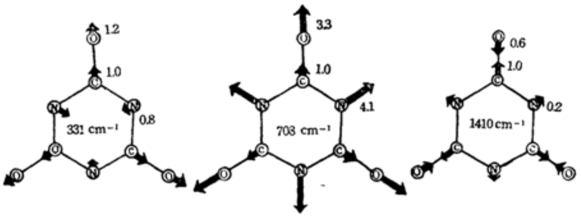

Fig. 2.—Calculated totally-symmetric vibrational frequencies and modes of the cyanuric acid ion.

If we chose 431 cm.$^{-1}$, some force constants would come out negative. Therefore we took

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(3) E. H. Wiebenga and N. F. Moermann, *Z. Krist.*, **99**, 217 (1938).

(4) G. Herzberg, "Raman and infrared spectra of polyatomic molecules," Van Nostrant, N. Y., (1945).

(5) Hibben, "Raman effect and its chemical application", Reinhold, N. Y., (1939).

(6) L. Kellner, *Proc. Roy. Soc. London*, **177**, 456 (1941).

331 cm.$^{-1}$ as the frequency of the third totally-symmetric vibration. The force constants calculated on the above assumptions are

$k$ (C—O) = $6.71\times10^5$ dyne/cm.,
$k$ (C—N) = $5.71\times10^5$ dyne/cm..

In Fig. 2, the calculated vibrational modes are shown for each frequency.

Comparing the above force constants with those already known for other molecules, the $k$ value for the c-o bond may be explained as the result of addition of a slight double-bond character to that of the formal single bond, and the $k$ value for the C—N bond caused by the actual bond having a more single-bond character than the formal one-and-half-bond. Thus the cyanuric acid ion gets some resonance contribution also from the keto-ionic structure as well as from the kekulé-like structures, as shown in Fig. 1.

Next, we applied the same consideration to the keto-formal structure (II) which is stable in acidic solution. Assuming also the symmetry $D_{3h}$ for this structure, the totally-symmetric vibrations are four in number theoretically, i. e. in addition to the three vibrational types mentioned above for the cyanuric acid ion there is one more totally-symmetric stretching vibration of the N—H bond.

With the same procedures the four totally-symmetric vibration frequencies belonging to the formula (II) in Fig. 1 were calculated, using the following force constants

$k$ (C=O) = $11.6\times10^5$ dyne/cm.,(5)
$k$ (C—N) = $4.85\times10^5$ dyne/cm.,(5)
$k$ (N—H) = $6.20\times10^5$ dyne/cm.,(5)
$\delta$ (∠NCN) = $0.23\times10^5$ dyne/cm.,(6)
$\delta$ (∠CNC) = $0.32\times10^5$ dyne/cm.,(6)

The resulting frequencies are

353 cm.$^{-1}$: deformation vibration,
769 cm.$^{-1}$: breathing vibration,
1811 cm.$^{-1}$: stretching vibration of the C=O bond,
3346 cm.$^{-1}$: stretching vibration of the N—H bond.

These frequencies are again very different from the observed Raman values 853, 1636, etc. In order to obtain a better agreement, we mnst adopt a larger and a smaller force constant for the C-N and the C=O bond respectively. The binding strength of the C-N bond in thit molecule should be larger than that of the formal C-N bond, and the C=O bond of it should be weaker than in the formal C=O bond. Accordingly some amount of the resonance contribution from the ionic structures (II)′ and (II)″ in Fig. 2 may be expected.

Although it is certain that cyanuric acid takes predominantly the keto-form in the acidic solution and enol-form in the alkaline solution, respectively, only the extreme structures (I) and (II) cannot explain the facts.

For example, the reported atomic distances in crystalline cyanuric acid are 1.28 A for the C-O bond and 1.37 A for the C-N bond,(3) both of which are intermediate between the normal single and the normal double bond lengths.

This fact is also confirmed by magnetic susceptibility measurements.(7) In the case of cyanuric acid in acidic or alkaline solution the structural contribution of the enol-or the keto-form appears much more dominant than in the case of crystal, depending on the $p$H value of the solution.

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(7) J. Maruyoshi, *J. Chem. Soc. Japan*, **71**, 627 (1950).