Fourier transform detection of laser-induced fluorescence from the CCN free radical

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The technique of high-resolution Fourier transform spectroscopy has been used to detect the laser-induced fluorescence spectrum of the CCN free radical. Emission from a single vibronic level in the $\tilde{A}\,^2\Delta$ state to the $\tilde{X}\,^2\Pi$ state yielded rotational constants for several vibronic levels of the ground state. From the analysis of the $0v_21$ levels the size of the Renner–Teller interaction was determined, yielding $\epsilon = 0.410$.

I. INTRODUCTION

The CCN radical is an unsymmetrical linear molecule with a $^2\Pi$ gound electronic state. It exhibits a fairly large Renner–Teller interaction and, consequently, has been the subject of several recent investigations. The original observation of CCN was made by Merer and Travis[1] in 1965. They observed the $\tilde{A}\,^2\Delta$–$\tilde{X}\,^2\Pi$, $\tilde{B}\,^2\Sigma^-$–$\tilde{X}\,^2\Pi$, and $\tilde{C}\,^2\Sigma^+$–$\tilde{X}\,^2\Pi$ bands in absorption following the photolysis of diazoacetonitrile. The recent extention of dye laser spectroscopic techniques into the blue region of the spectrum has made additional investigation of CCN worthwhile. In the first such study Kakimato and Kasuya[2] reanalyzed the 000–000 band of the $\tilde{A}\,^2\Delta$–$\tilde{X}\,^2\Pi$ system. They obtained improved fine structure rotational, and lambda doubling constants. Subsequently, Kawaguchi *et al.*[3] extended the analysis to the 010–010 and 020–020 sequence bands in the bending vibration. However, like Merer and Travis[1] they could find only two of the three Renner–Teller components of the 010 level of the ground state, and hence, were unable to make a complete analysis of the Renner–Teller interaction.

No conventional emission spectrum of CCN has been analyzed, however, Hakuta and Uehara[4] found that the 4658 Å line of an argon ion laser coincides with two rotational transitions in the 010–010 band of the $\tilde{A}\,^2\Delta$–$\tilde{X}\,^2\Pi$ system. They resolved the resultant laser-induced fluorescence with a monochromator and obtained ground state vibrational frequencies. These frequencies were not in complete agreement with the values obtained by Bondybey and English[5] in a matrix isolation experiment. The gas phase value of ν_1 is 200 cm^{-1} higher than the matrix value—a much larger than normal matrix shift for a vibrational frequency. Very recently Suzuki, Saito, and Hirota have observed excited state microwave–optical double resonances in the $\tilde{A}\,^2\Delta$–$\tilde{X}\,^2\Pi$ transition.[6]

The results of Hakuta and Uehara[4] prompted our interest in CCN. They had obtained gas-phase vibrational frequencies by the use of a small monochromator to disperse the fluorescence, but their maximum resolution of about 4 cm^{-1} was insufficient for a rotational analysis. To obtain the necessary resolution we repeated their experiment, but used the Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak to resolve the fluorescence.

Previous studies of laser-induced fluorescence using Fourier transform detection have involved species such as I_2,[7] Te_2,[8] and Na_2[9] which can be obtained in relatively high concentration in a cell or a heat pipe oven. The equivalent experiment for a free radical, such as CCN, is more difficult, due to the problem of maintaining a sufficiently high concentration of the molecule in the region of interaction with the laser beam. The molecular concentration in an I_2 cell at room temperature is about 10^{16} molecules/cm^3. For free radicals concentrations four to six orders of magnitude less than this are typical. In our first efforts to detect laser-induced fluorescence of free radicals by Fourier transform spectroscopy the $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ transition of SrOH[10] and the $\tilde{A}\,^2\Delta$–$\tilde{X}\,^2\Pi$ transition of CCN served successfully as our test cases. The technique of Fourier transform detection of laser-induced fluorescence holds considerable promise for the simplification of complex polyatomic emission spectra.

In the present study we used a bandpass filter to block scattered laser light and as a result only emission to excited vibrational levels of the ground state was observed. A total of five bands were rotationally analysed yielding frequencies for the two stretching modes ν_1 and ν_3. The observation of a progression in the bending mode $0v_21$ for the $\tilde{X}\,^2\Pi$ state made possible the direct determination of ϵ and ω_2 for the first time. The value for ω_2 is in excellent agreement with that calculated by Merer and Travis[1] while ϵ is slightly different due to the neglect of the small contribution from the parameter g_K[11] in the original analysis.

II. EXPERIMENTAL

The CCN radical was continuously produced in a glass reaction tube. Fluorine atoms, produced by microwave discharge of CF_4, were reacted with acetonitrile.[2–4] The pressure of CF_4 was 350 mTorr and the amount of acetonitrile, a few mTorr, was adjusted to maintain the chemiluminescent reaction in the center of the tube. The 4658 Å output of an argon ion laser (Coherent Innova 90-4, 200 mW power) was reflected from a small pick-off mirror and focused down the length of the reaction tube. The laser induced fluorescence was gathered with a lens placed just behind the mirror and focused onto the input aperture of the Fourier transform spectrometer. The red chemiluminescence from the reaction was blocked by a copper sulfate filter and a long-wavelength pass filter (Schott GG 495) was used to block scattered laser light. A total of 42 scans were co-added in 2½ h of recording. The spectrometer was set to have a resolution of 0.05 cm^{-1}, the estimated Doppler width of the rotational lines. The de-

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tectors were two cooled GaAs (RCA C31034) photomultiplier tubes.

III. OBSERVATIONS AND ANALYSIS

The interferogram was transformed by standard methods to yield the spectrum, which covers the range from 18 000 to 20 500 cm^{-1}. At low resolution ($\sim 10\ cm^{-1}$) nine bands are discernible (see Fig. 1). The vibronic assignments for the six strongest bands are given in Fig. 1. These assignments are based on the results of Hakuta and Uehara,[4] and our subsequent high-resolution analysis of five of these bands confirms their assignments.

The three strongest vibronic bands 010Φ–011Δ, 010Φ–012Δ, and 010Φ–110Δ, contain emission from both resonantly excited and collisionally populated rotational levels. A section from the 010Φ–011Δ band is shown in Fig. 2. The 4658 Å line of an Ar^+ laser is coincident with two transitions in the 010Φ–010Δ band, R_1 (23.5) and ${}^sR_{21}$ (12.5). A total of six lines, P, Q, and R to each spin-orbit component of the ground electronic state, are seen from each resonantly excited rotational level. The resonant lines are typically a factor of 4 to 10 stronger than the lines populated by collisional relaxation as in Fig. 2. The assignment of the resonant lines is easy and the other members of each branch can then be assigned by counting. A fourth resonantly excited band 010Φ–031Δ was observed. In this case just the resonant lines appeared with reasonable intensity and only a few very weak transitions from relaxation populated levels could be measured.

These four bands were fitted using the matrix elements of Kawaguchi *et al.*[3] The common excited state 010Φ has been studied before at high resolution.[3] Our constants were essentially the same for the excited 010Φ level as those determined previously[3] and for the final fits the constants were fixed to the values obtained by Kawaguchi *et al.*[3] For most bands lines from all 12 branches (P_1, Q_1, R_1, P_2, Q_2, R_2, P_{12}, Q_{12}, R_{12}, P_{21}, Q_{21}, and R_{21}) were observed, although in many branches only the resonant line was sufficiently strong to be recorded. The list of observed transition wave numbers is given in Table I (see PAPS Ref. 12). Each was weighted according to its estimated singal-to-noise ratio unless it was blended, in which case a lower weight was used.

For each band five constants were required, a transition energy (T), a spin-orbit coupling constant (A), a rotational constant (B) and its centrifugal distortion (D), and a spin-rotation constant (γ). The values for these parameters are all listed in Table II, together with one standard deviation error estimates from the least-squares fit. Both the 011Δ and 012Δ vibronic level are well behaved and the constants are quite similar to those for 010Δ.[3] The 110Δ level shows clear evidence of local perturbations of $J'' = 9.5$ and 10.5 in the F_2 component and $J'' = 20.5$ in the F_1 component. It proved impossible to fit any of the F_2 levels below $J'' = 9.5$ with the rest of the band so these lines were excluded from the final fit. The effects of the perturbation also appear in the centrifugal distortion and spin-rotation constants, which are quite different from the other $v_1 1 v_2 \Delta$ levels. Although the 110Δ level is only 2240 cm^{-1} above 000Π it was not possible to identify which vibronic level is causing the perturbation. This is due to the rather large Renner–Teller interaction ($\epsilon = 0.41$) which makes it very difficult to accurately calculate the positions of the excited bending mode levels.

In the excited $\tilde{A}\ ^2\Delta$ state the 010Π level is populated by collisional relaxation. Two weak bands originating in this level were observed. Only for the 010Π–011$\kappa\Sigma^+$ band was the signal-to-noise ratio high enough to permit a rotational analysis. The Q branch lines could be identified without difficulty and their assignment was adjusted in order to reproduce the observed P branch bandheads. The excited state parameters were fixed at the values obtained by Kawaguchi *et al.*[3] and only the ground state parameters were allowed to vary. Only one assignment reproduced the P branch heads

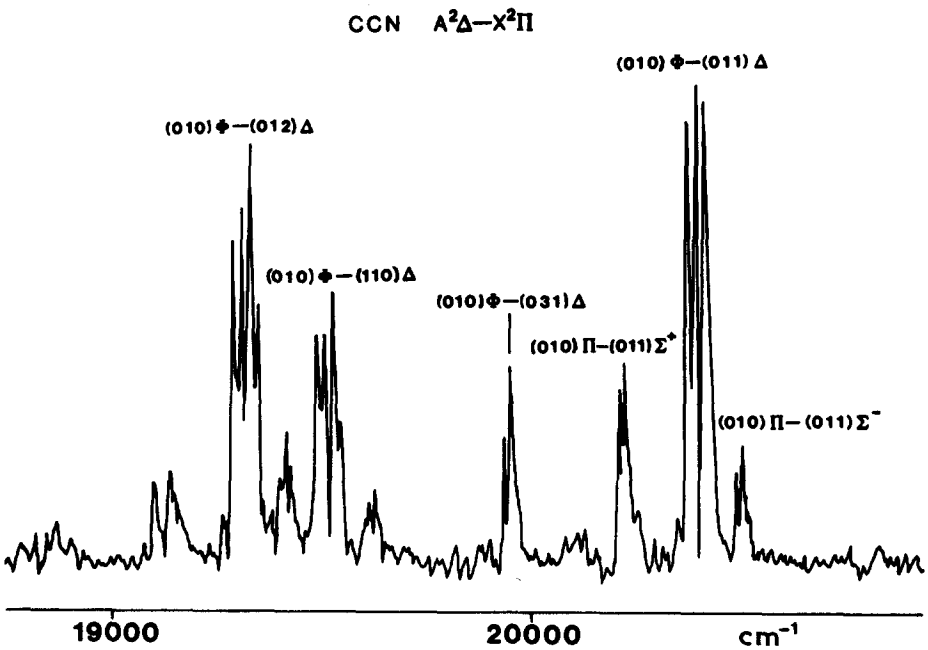

FIG. 1. Observed vibronic bands of the $\tilde{A}\ ^2\Delta$–$\tilde{X}\ ^2\Pi$ transition of CCN at low resolution. Excitation is in the 010Φ–010Δ band offscale to the right at 21 219 cm^{-1}. The relative intensities of the bands are distorted by the filters used to block scattered laser light and chemiluminescence.

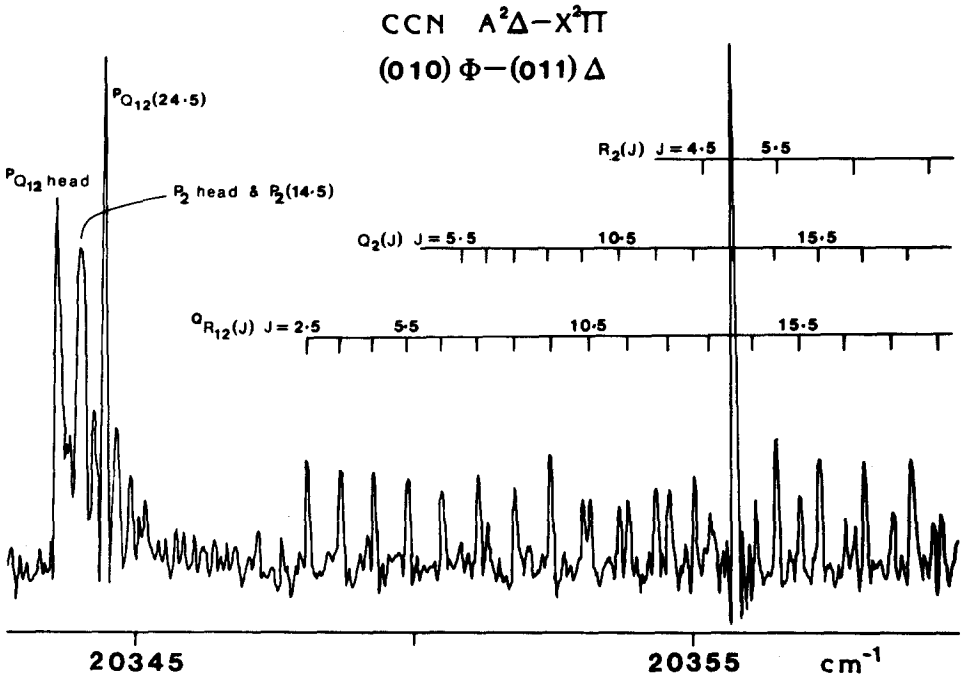

FIG. 2. A section of the 010Φ–011Δ band at high resolution. The spectrum consists of both strong resonantly excited lines [e.g., $Q_2(13.5)$] and weaker lines produced by rotational relaxation in the excited state.

correctly. In addition this assignment predicted several P and R branch lines which were then included in the analysis.

The one unsatisfactory feature is that the centrifugal distortion parameter D is negative for the $011\kappa\Sigma^+$ level. One possible explanation is our neglect of K-type resonance which was included in the analysis of NCO.[13] This was considered to be a possible contribution to the variation in D between the different components of the 010 levels by Kawaguchi *et al.*[3]

IV. DISCUSSION

The results of the fit of the five observed vibronic transitions may be used to calculate vibrational and Renner–Teller parameters for CCN. Transitions involving one and two quanta of ν_3'' were observed and from this $\omega_3 = 1069.007(4)$ and $x_{33} = -4.109(2)$ may be derived (Table III). The observed vibrational frequencies are consistent with those of Hakuta and Uehara[4] and Bondybey and English.[5] The difference between the $\tilde{X}\,^2\Pi$ 010Δ and 110Δ levels (Table II) provides an estimate of $\nu_1'' = 1915.7658(44)$. This value of ν_1 is in agreement with the value of Hakuta and Uehara[4] but is 199 cm^{-1} higher than the Ar matrix value[5] of 1717 cm^{-1}. Note that since ν_1'' and ν_3'' were not directly observed in our measurements systematic errors of a few cm^{-1} are present because not all of the x_{ij}'s are known.

The Renner parameter ϵ can be evaluated if all three vibronic components of a $v_1 1 v_3$ level are observed together with at least one member of a vibrational sequence in ν_2. Good data is available for all the necessary levels for $0v_21$ except for the $\mu\Sigma^-$ component. The intensity of the transitions to this level should be about the same as those to the 011 $\kappa\Sigma^+$ level, but is reduced by the red pass filter used to block scattered laser light. From the high-resolution spectrum the origin of the 010Π–$011\mu\Sigma^-$ transition was estimated to be 20465.4 ± 0.5 cm^{-1} with the help of constants based on the other components of the 011 level. The $\tilde{A}\,^2\Delta$ 010Φ–$\tilde{A}\,^2\Delta$ 010Π splitting[1] of 13.39 cm^{-1} results in a band origin of 948.7 cm^{-1} for 011 $\kappa\Sigma^+$ relative to $\tilde{X}\,^2\Pi$ 010Δ.

The positions of the levels in terms of the vibronic parameters are given by Hougen[14] and for the levels of interest here, relative to 001, they are as follows:

$$E(031\mu\Delta) = 4\omega_2 - \epsilon^2\omega_2/2 - \sqrt{(A^2 + 12\epsilon^2\omega_2^2)}/2 + 2g_K, \quad (1a)$$

$$E(011\kappa\Sigma^+) = 2\omega_2 - \epsilon^2\omega_2/4 + \sqrt{A^2 + 4\epsilon^2\omega_2^2)}/2, \quad (1b)$$

$$E(011\Delta) = 2\omega_2 - 3\epsilon^2\omega_2/4 + 2g_K, \quad (1c)$$

TABLE II. Molecular constants for the $\tilde{X}\,^2\Pi$ state of CCN (cm^{-1}).

	011Δ	$011\kappa\Sigma^+$	012Δ	110Δ	$031\mu\Delta$
A	36.018 5(10)[a]	...	35.817 22(24)	36.203 1(56)	9.775(16)
B	0.398 628 7(36)	0.396 111(35)	0.396 148 1(79)	0.398 422(28)	0.404 432(68)
$D \times 10^7$	2.678(40)	−8.79(50)	2.715(79)	1.12(35)	1.85(85)
γ	−0.006 91(12)	0.009 66(15)	−0.003 25(22)	0.000 73(76)	0.003 64(65)
T[b]	1060.788 1(7)	1217.425[c]	2113.353 1(17)	1915.765 8(44)	1491.649 9(111)

[a] The numbers in parentheses represent one standard deviation error estimates in the last quoted figure.
[b] Energy relative to 010Δ.
[c] Calculated using the $\tilde{A}\,^2\Delta$ 010Φ–$\tilde{A}\,^2\Delta$ 010Π splitting of 13.39 cm^{-1} (Refs. 1 and 3).

TABLE III. Summary of vibrational, Renner–Teller, and spin-orbit constants for $\tilde{X}\,^2\Pi$ state of CCN (in cm^{-1}).

$\omega_3 = 1069.007(4)$	$\epsilon = 0.410$
$x_{33} = -4.109(2)$	$\epsilon\omega_2 = 132.8$
$\nu_1 = 1915.765\,8(44)$	$g_K = 2.5$
$\omega_2 = 324.0$	$A_{true} = 41.76$

$$E(011\mu\Sigma^-) = 2\omega_2 - \epsilon^2\omega_2/4 - \sqrt{(A^2 + 4\epsilon^2\omega_2^2)}/2, \quad (1d)$$

where ω_2 and ϵ are the usual vibrational frequency and Renner parameter, A is the "true" spin-orbit parameter and g_K is the K dependent correction term introduced by Brown.[11] All anharmonicity terms have been neglected. The true value for A in $0v_21$ levels can be calculated from the effective one using the expression from Brown[11] and Aarts[15]:

$$A_{eff} = A_{true}[1 - \epsilon^2 K(K+1)/8 + K\eta]. \quad (2)$$

The term η represents interactions with other $^2\Sigma$ electronic states and has been determined by Kawaguchi *et al.*[3] for $0v_20$, $\eta = -0.0058$. The observed numerical values for Eqs. 1(a)–1(d) are 1491.6351, 1217.425, 1060.788 (Table II), and 948.7 cm^{-1}, respectively, measured relative to the 010Δ level. Taking the values of Merer and Travis[1] of $\omega_2 = 325$ cm^{-1} and $\epsilon = 0.44$, as initial estimates gives $A_{true} = 42.72$ cm^{-1} from Eq. (2). New values of ω_2 and ϵ can then be found from the observed energy level spacings. These give a new value for A_{true} and after two more cycles the values of the Renner–Teller parameters converged to

$$\omega_2 = 324.0\ cm^{-1}, \quad \epsilon = 0.410,$$

$$A_{true} = 41.76\ cm^{-1}, \quad g_K = 2.5\ cm^{-1}.$$

The value for ω_2 is very close to $\omega_2'' = 325$ cm^{-1} calculated by Merer and Travis[1] from the $\tilde{C}\,^2\Sigma^+$–$\tilde{X}\,^2\Pi$ analysis. The agreement is remarkably good considering the approximations they had to make in order to calculate ω_2 for the $\tilde{C}\,^2\Sigma^+$ state from the observed l-type doubling.[1] The Renner parameter, $\epsilon = 0.410$, is somewhat smaller than the previous value of 0.44.[1] This is partly due to $\epsilon\omega_2 = 132.8$ cm^{-1} being smaller for the $0v_21$ level than $0v_20$ level.[4] In addition the previous workers found only one of the two Σ components and were forced to neglect the g_K term when calculating the Renner interaction parameter. The effect of the g_K term is to shift the $^2\Delta$ component, in this case up by 5 cm^{-1}, accounting for most of the discrepancy. The value of g_K is comparable to other similar molecules,[11] for example, $g_K = 2.5$ cm^{-1} in the $\tilde{X}\,^2\Pi$ state of NCO and $g_K = 3.64$ cm^{-1} in the $\tilde{A}\,^3\Pi$ state of NCN.

A_{true} is 1 cm^{-1} less than for $0v_20^3$ indicating a rather large vibrational dependence of the spin-orbit splitting. The value of the spin-orbit coupling constant for the $\tilde{X}\,^2\Pi\ 031\mu\Delta$ level is given by[14,16]

$$A_{eff} = \epsilon^2\omega_2 K A_{true}/\sqrt{(A^2 + 12\epsilon^2\omega_2^2)}. \quad (3)$$

Substituting the values from Table III predicts $A_{eff} = 9.96$ cm^{-1} compared to the observed 9.78 cm^{-1}.

V. CONCLUSION

The rotational structure for several excited vibrational levels of the ground electronic state of CCN was analyzed. Vibrational and Renner–Teller constants were derived for the $\tilde{X}\,^2\Pi$ state.

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[12] See AIP document no. PAPS JCPSA-86-3078-9 for 9 pages of Table I (Observed transitions in the $\tilde{A}\,^2\Delta$–$\tilde{X}\,^2\Pi$ band of CCN). Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
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