A Fermi Resonance with ν_6 of Acetonitrile

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The rotation-vibration spectrum of ν_6 of acetonitrile measured by Nakagawa *et al.* has been reanalyzed by taking account of the Fermi resonance between the states $|v_6=1>$ and $|v_7=1, v_8=1>$. The previous assignment of Q branches by Amat *et al.* has been revised on the basis of the obtained values of band constants. The following band constants have been determined for the ν_6 band: $\nu_0=1447.9$ cm^{-1}, $\zeta=-0.305$ and $\alpha^A=0.046$ cm^{-1}. From the value of the resonance operator, the magnitude of the cubic force constant k_{678} has been estimated to be about 30 cm^{-1}.

Rotation-vibration spectra of acetonitrile CH_3CN have been studied by Parker, Nielsen, and Fletcher[1] and Nakagawa and Shimanouchi,[2] and anomalous rotational structures have been found in the ν_6 perpendicular band. Amat and Nielsen[3] interpreted the anomaly to be due to the Fermi resonance between the states $|v_6=1>$ and $|v_7=1, v_8=1>$ and made an assignment of observed Q branches. In the present study, the ν_6 band region in the spectra of Nakagawa and Shimanouchi[2] was reanalyzed and Amat's assignment was revised on the basis of the obtained values of band constants.

Spectral Analysis and Discussion

As shown in Fig. 1, the observed spectrum in the region 1300—1600 cm^{-1} consists of two series of Q branches (ν^+ and ν^-), higher- and lower-wave number components of the Fermi doublet. We have three possible vibrational states which can be coupled with and perturb the $|v_6=1, l_6=\pm1>$ state through Fermi-resonance operators; namely $|v_7=1, l_7=\mp1, v_8=1, l_8=\mp1>$, $|v_8=4, l_8=\mp2>$ and $|v_8=4, l_8=\pm4>$, which have rotation-vibration energies close to that of the $|v_6=1, l_6=\pm1>$ state. It has become evident, from the obtained values of the band constants, that the perturber is the $|v_7=1, l_7=\mp1, v_8=1, l_8=\mp1>$ state. In assigning observed Q branches, however, there are two possible K-numberings (Assignment I and Assignment II) as shown in Table 1; they differ in the assigned $K\Delta K$ numbers by one in the ν^- component. Assignment II corresponds to Amat's assignment.[3] Analyses of the band system were made according to the two assignments.

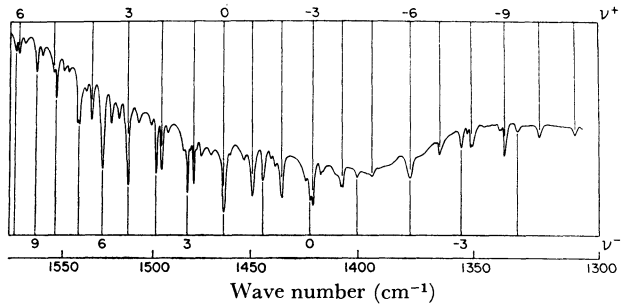

Fig. 1. Infrared spectrum of the ν_6 region of CH_3CN (Ref. 2). Numbers shown above and below the spectrum are $K\Delta K$ numbers for ν^+ and ν^- according to Assignment I.

In calculating the unperturbed band constants, the following matrix was set up for each K value

$$\begin{bmatrix} E^0(v_6=1, l_6=\pm1, K) & W \\ W & E^0(v_7=1, l_7=\mp1, v_8=1, l_8=\mp1, K) \end{bmatrix},$$

where E^0 denotes the unperturbed energy and W the matrix element of the Fermi-resonance operator. The unperturbed band constants and the resonance operator were determined by solving the above matrix and fitting observed wavenumbers to the wave number equation by the method of least squares. The results are given in Table 2. The values of ν_0, ζ, and α^A ($=A''-A'$) were calculated by assuming $B'=B''=0.3068$ cm^{-1} and $A''=5.280$ cm^{-1}.[4] From the ζ_7 value (0.422)[2] and the ζ value $[-(\zeta_7+\zeta_8)]$ of the $\nu_7+\nu_8$ band, we obtain $\zeta_8=0.863$ for Assignment I and $\zeta_8=0.764$ for Assignment II. Venkateswarlu *et al.*[5] have obtained $\zeta_8=0.88$ from microwave studies. The good agreement between the ζ_8 value for Assignment I and the microwave value is an evidence that favors Assignment I. From the ζ_6 and ζ_8 values of the present study and the ζ_5 and ζ_7 values previously determined,[2] we can check the ζ-sum rule ($\sum_t \zeta_t = 1+B/2A$); $\sum_t \zeta_t=1.042$ for Assignment I and $\sum_t \zeta_t=0.898$ for Assignment II, while $1+B/2A=1.029$. Agreement between the left- and right-hand sides is much better for Assignment I than for Assignment II.

Values of the rotation-vibration coupling constant α^A for localized vibrations, *e.g.* CH_3 stretching and CH_3 bending vibrations of CH_3X and CH_3CN, are expected to be similar for the same vibrational modes.[6,7] α^A values for the CH_3 rocking, and CH_3 asymmetric stretching vibrations of CH_3CN are, in fact, close to the corresponding values for CH_3Cl, CH_3Br and CH_3I. The α^A value for ν_6 of CH_3CN (CH_3 asymmetric deformation) was determined to be 0.046 cm^{-1} for Assignment I and 0.028 cm^{-1} for Assignment II. The former is much closer than the latter to the corre-

1) F. W. Parker, A. H. Nielsen, and W. H. Fletcher, *J. Mol. Spectrosc.*, **1**, 107 (1957).

2) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 513 (1962).

3) G. Amat and H. H. Nielsen, "Molecular Orbitals in Chemistry, Physics and Biology," ed. by P.-O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 293.

4) M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **79**, 54 (1950).

5) P. Venkateswarlu, J. G. Baker, and W. Gordy, *J. Mol. Spectrosc.*, **6**, 215 (1961).

6) Y. Morino and J. Seto, Annual Meeting of the Chemical Society of Japan, Tokyo, 1958.

TABLE 1. Q-BRANCHES OF THE FERMI DIAD ν_6 AND $\nu_7 + \nu_8$ OF CH_3CN

	Assignment I[a]				Assignment II			
	ν^+		ν^-		ν^+		ν^-	
	ν_{obs}[b]	$\Delta\nu$[c]	ν_{obs}[b]	$\Delta\nu$[c]	ν_{obs}[b]	$\Delta\nu$[c]	ν_{obs}[b]	$\Delta\nu$[c]
$^PQ_{11}$	1309.39	0.22			1309.39	0.42		
$^PQ_{10}$	1323.29	−0.02			1323.29	0.13		
$^PQ_9$	1337.01	−0.37			1337.01	−0.29		
$^PQ_8$	1350.63[d]	−0.76			1350.63[d]	−0.76		
$^PQ_7$	1364.39[d]	−0.95			1364.39[d]	−1.05		
$^PQ_6$	1377.60[d]	−1.64			1377.60[d]	−1.84		
$^PQ_5$	1393.33	0.22			1393.33	−0.07	1331.84	−0.41
$^PQ_4$	1407.06	0.09	1331.84	−0.04	1407.06	−0.27	1354.77	−0.18
$^PQ_3$	1420.88	0.01	1354.77	−0.03	1420.88	−0.36	1377.60	0.14
$^PQ_2$	1434.82	−0.03	1377.60	0.00	1434.82	−0.34	1400.36	0.60
$^PQ_1$	1449.14	0.10	1400.36	0.19	1449.14	−0.03	1422.30	0.51
$^RQ_0$	1463.34	−0.28	1422.30	−0.02	1463.34	−0.06	1443.88	0.48
$^RQ_1$	1478.81	−0.12	1443.88	0.16	1478.81	0.50	1463.34	−0.78
$^RQ_2$	1495.56	0.08	1463.34	−0.51	1495.56	0.52	1482.27	−0.57
$^RQ_3$	1513.85	0.06	1482.27	0.08	1513.85	−0.44	1498.66	−0.18
$^RQ_4$	1533.95	0.01	1498.66	−0.00	1533.95	−0.94	1513.85	0.56
$^RQ_5$	1555.53	0.02	1513.85	0.16	1555.53	−0.37	1527.81	0.68
$^RQ_6$	1577.98	−0.01	1527.81	0.04	1577.98	0.97	1541.38	0.69
$^RQ_7$			1541.38	0.12			1554.33	0.25
$^RQ_8$			1554.33	−0.01			1567.08	−0.28
$^RQ_9$			1567.08	−0.06			1579.67	−0.87
$^RQ_{10}$			1579.67	−0.05				

a) More likely assignment.
b) Observed wave number (cm^{-1}).
c) $\Delta\nu = \nu_{obs} - \nu_{calc}$.
d) Omitted from the least squares calculation.

sponding values[8,9] of 0.048 cm^{-1}, 0.048 cm^{-1} and 0.046 cm^{-1} determined for CH_3Cl, CH_3Br, and CH_3I, respectively. This is another basis for preferring Assignment I to Assignment II.

By comparing the results obtained for both assignments, it is now concluded that Assignment I is a more likely alternative; the results for Assignment I will therefore be used in subsequent parts of this paper. The better agreement between the observed and calculated wavenumbers for Assignment I than Assignment II (see Table 1) may also support this conclusion. In order to check the conclusion, approximate intensity ratios of the Q branches for the ν^+ and ν^- components with the same $K\Delta K$ numbers were calculated for the two assignments. However, a definite comparison could not be made due to overlapping of some of the Q branches and another kind of perturbation.

The unperturbed band origin of ν_6 was determined to be 1447.9 cm^{-1}. This wave number is about 6 cm^{-1} lower than the wave number[1,2] previously obtained without taking account of the Fermi resonance. From the wave number of the band origin for $\nu_7+\nu_8$ and those for ν_7 and ν_8,[2] the anharmonic term[10] $x_{78}+x_{l_7l_8}=-0.8$ cm^{-1} is obtained.

Assuming that the Fermi-resonance operator W is

TABLE 2. BAND CONSTANTS OF THE ν_6 AND $\nu_7 + \nu_8$ BANDS OF CH_3CN IN cm^{-1}

Constant	Assignment I[a]		Assignment II	
	ν_6	$\nu_7+\nu_8$	ν_6	$\nu_7+\nu_8$
$\nu_0 + A'(1-\zeta)^2 - B'$	1456.54±0.07	1429.40±0.10	1461.34±0.21	1445.46±0.28
$2[A'(1-\zeta)-B']$	13.051±0.008	23.67±0.02	13.569±0.024	22.17±0.05
$(A'-B')-(A''-B'')$	−0.046±0.001	0.033±0.007	−0.028±0.004	−0.070±0.016
$\lvert W\rvert$	15.57±0.06		6.07_5±0.23	
ν_0[b]	1447.93	1401.97	1452.07	1420.86
ζ[b]	−0.305	−1.285	−0.350	−1.186
α^A[b]	0.046	−0.033	0.028	0.070

a) More likely assignment.
b) Calculated by assuming $B'=B''=0.3068$ cm^{-1} and $A''=5.280$ cm^{-1} (Ref. 4).

7) S. Reichman and J. Overend, *J. Chem. Phys.*, **48**, 3095 (1968).
8) Y. Morino and J. Nakamura, This Bulletin, **38**, 443 (1965).
9) H. Matsuura and J. Overend, *J. Chem. Phys.*, to be published.
10) H. H. Nielsen, "Handbuch der Physik," Vol. 37, ed. by S. Flügge, Springer-Verlag, Berlin (1959), p. 173.

determined by the following anharmonic term of the intramolecular potential

$$V = hck_{678}[q_{6a}(q_{7a}q_{8a}-q_{7b}q_{8b}) - q_{6b}(q_{7a}q_{8b}+q_{7b}q_{8a})],$$

we find the following non-zero matrix element

$$\langle v_6, l_6, v_7, l_7, v_8, l_8 | V/hc | v_6-1, l_6\pm1, v_7+1, l_7\pm1, v_8+1, l_8\pm1\rangle = \pm(1/4\sqrt{2})k_{678}[(v_6\mp l_6)(v_7\pm l_7+2)(v_8\pm l_8+2)]^{1/2}.$$

Accordingly, from the $|W|$ value obtained in the present analysis, the magnitude of the cubic force constant k_{678} is estimated to be $|k_{678}|=2|W|=31$ cm^{-1}.

It has been found in the course of the analysis that there is another kind of perturbation, though much weaker than the one described above, for ${}^PQ_6-{}^PQ_8$ in the ν^+ component; the observed wave numbers deviate systematically from the calculated wave numbers (see Table 1). Amat and Nielsen[3] explained it as due to a Coriolis interaction between the states $|v_8=1\rangle$ and $|v_6=1\rangle$. The observed wavenumbers for these Q branches were omitted in determining the band constants given in Table 2.

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After this work was completed, the author has been informed by Professor. G. Amat that J. L. Duncan, D. Ellis, and I. J. Wright [*Mol. Phys.*, **20**, 673 (1971)] independently studied the same subject and obtained essentially the same results.