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VIBRATION-ROTATION INFRARED SPECTRUM OF ν_6 OF ACETONITRILE. FERMI AND CORIOLIS RESONANCES WITH $\nu_7+\nu_8$ AND ν_3

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Vibration-rotation infrared spectrum of ν_6 of acetonitrile was measured with a resolution of 0.08 cm^{-1}. The spectrum was heavily perturbed by a Fermi resonance with $\nu_7+\nu_8$ and a Coriolis resonance with ν_3. The analysis gave values, more precise than before, of the parameters for these states along with the interaction parameters.

Acetonitrile or methyl cyanide, CH_3CN, is one of the typical symmetric-top molecules and its vibration-rotation spectra have been extensively studied.[1-8] Of the fundamental bands of this molecule, ν_6 (E; CH_3 degenerate deformation) is an interesting band from the viewpoint of spectral analysis, because this band is strongly perturbed by a Fermi resonance with $\nu_7+\nu_8$ (E) and by a Coriolis interaction with ν_3 (A_1). The vibration-rotation spectrum of ν_6 has been in fact analyzed by taking account of these interactions.[5,6] The resolution of the previous spectra was, however, not high enough to enable ones to investigate in full the band system ν_6, $\nu_7+\nu_8$, and ν_3. Accordingly, in the present study, the vibration-rotation infrared spectrum of acetonitrile was measured with a resolution higher than before and analyzed in detail to provide more precise values of parameters for ν_6, $\nu_7+\nu_8$, and ν_3 and for the interactions involved.

The infrared spectrum of gaseous acetonitrile was recorded on a JEOL JIR-40X Fourier transform infrared spectrometer. Gas pressures of 8–15 Torr were utilized in a 1-m cell. The spectrometer was flushed with dry nitrogen gas throughout the measurement to eliminate atmospheric water-vapor absorptions. The practical spectral resolution was about 0.08 cm^{-1}, which was much better than 0.4 or 0.3 cm^{-1} in the previous measurements.[3,6] The observed wavenumbers were calibrated by using the IUPAC wavenumber tables.[9]

Figure 1 shows the vibration-rotation spectrum of the band system ν_6, $\nu_7+\nu_8$, and ν_3. About 1250 lines were observed in the region between 1640 and 1250 cm^{-1}. The spectral analysis was started by assigning the Q branches of the perpendicular transitions. The two series of the Q branches due to the two components of the $\nu_6/\nu_7+\nu_8$ Fermi diad were assigned unambiguously on the basis of the three-fold intensity alternation and the number of missing lines of the associated P and R branches. The present K-assignment of the Q branches is in agreement with our[5] and Duncan's[6] previous assignments.

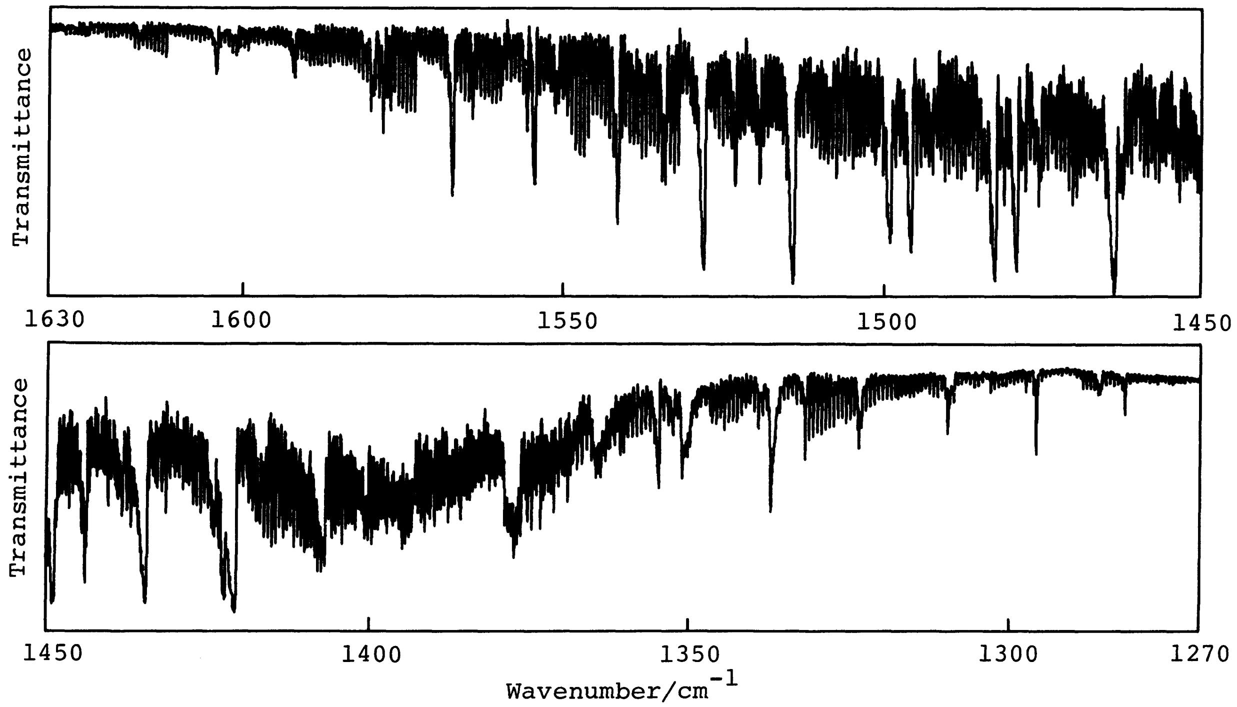

Fig. 1. Infrared spectrum of the ν_6 band region of gaseous CH_3CN.

The P- and R-branch lines were identified by tracing series of transition lines of spacing $2B \approx 0.6$ cm^{-1}. The following subband branches were finally identified and assigned: ${}^{P}P_K(J)^+$ with K=1–13, ${}^{R}R_K(J)^+$ with K=0–3 and 6, ${}^{R}P_0(J)^+$, ${}^{P}P_K(J)^-$ with K=1–3 and 6, and ${}^{R}R_K(J)^-$ with K=2–13, where superscripts + and - imply the higher- and lower-wavenumber components of the $\nu_6/\nu_7+\nu_8$ Fermi diad. Each of the subbands was analyzed to give the effective rotational constant B'_{eff}. Variation of the B'_{eff} value with the upper-state quantum number $K'\ell'$ is a criterion of vibrational and/or rotational perturbations involved in the band system.[10,11) In the higher component of the Fermi diad, the steadily decreasing B'_{eff} value with increasing $K'\ell'$ until -5 jumps up sharply at $K'\ell'=-4$, and beyond this point, the B'_{eff} value decreases as $K'\ell'$ increases. This observation indicates that an energy-level crossing with another state occurs between $K'\ell'=-5$ and -4 through a Coriolis-type interaction. This spectral perturbation is accounted for by the xy-type Coriolis interaction between ν_6 and ν_3. The same type of interaction has been observed for acetonitrile-d_3.11) The effect of the Fermi resonance between ν_6 and $\nu_7+\nu_8$ is not clearly indicated by the B'_{eff}-value variation, because the rotational constants B_6 for ν_6 and B_{78} for $\nu_7+\nu_8$ are not much different from each other.

In the band system ν_6, $\nu_7+\nu_8$, and ν_3, the vibration-rotation energy levels are heavily perturbed by the Fermi and Coriolis resonances mentioned above. The perturbed energies were obtained by solving successive (5×5)-dimensional energy matrices with the unperturbed energies in diagonal terms and the interaction parameters in off-diagonal terms. The matrix relevant to the present band system is similar to that for the band system ν_6 (E), $\nu_4+\nu_8$ (E), and ν_3 (A_1) of acetonitrile-d_3.11) In the course of the calculation, it was found that the observed wavenumbers of some of the subbands deviated systematically from the calculated ones. Accordingly, the largely deviating subbands $^{P}P_1(J)^+$, $^{P}P_6(J)^+$, $^{R}R_0(J)^+$, $^{R}P_0(J)^+$, $^{P}P_1(J)^-$, and $^{P}P_2(J)^-$ were omitted from the observed data in the subsequent least-squares adjustment of the spectroscopic parameters. Nevertheless, the wavenumbers of several subbands still deviated more or less.

The $v_7=1,v_8=1$ state has three components of A_1, A_2, and E species. Possible interactions associated with the first and second components were all neglected in the present analysis. Furthermore, the energy levels of the $v_8=4$ state with A_1 and two E species are close to those of the $v_6=1$ and the $v_7=1,v_8=1$ states. Thus, various types of Fermi and Coriolis interactions among these levels may perturb the spectrum in a complicated manner. The minor spectral deviations observed in the band system ν_6, $\nu_7+\nu_8$, and ν_3 are ascribable to the interactions which were neglected in the analysis. Identification of the origins of these deviations is practically impossible, because spectroscopic information to locate the perturbing levels is not available at present. Further comprehensive studies are required to investigate in full the band system of all coupling states.

The parameters for ν_6, $\nu_7+\nu_8$, and ν_3 and the interaction parameters were finally determined, as listed in Table 1, from a total of about 700 vibration-rotation transition wavenumbers. The above considerations on the various possible interactions indicate that the determined values of the parameters may involve

Table 1. Parameters for the ν_6, $\nu_7+\nu_8$, ν_3, and ground states of CH_3CN a)

Parameter	ν_6	$\nu_7+\nu_8$	ν_3	Ground state
$(\nu_0)_v$ b)	1448.007(8) c)	1410.605(9)	1381.78(16)	0
A_v	5.20459(9)	5.2679(6)	5.267 d)	5.247 e)
B_v	0.307105(10) f)	0.307605(14)	0.3074(2) f)	0.30684225 g)
$(A\zeta_t^{(z)})_v$	-1.6458(2)	-6.8892(3)	–	–
$(D_J)_v$	$1.24(5)\times10^{-7}$	$=(D_J)_0$	$=(D_J)_0$	1.2691×10^{-7} g)
$(D_{JK})_v$	$5.34(7)\times10^{-6}$	$=(D_{JK})_0$	$=(D_{JK})_0$	5.9180×10^{-6} g)
$(D_K)_v$	$9.12(4)\times10^{-5}$	$6.6(14)\times10^{-5}$	$=(D_K)_0$	9.473×10^{-5} h)
$(\eta_{tJ})_v$	$-5.4(5)\times10^{-6}$	0	–	–
$(\eta_{tK})_v$	$-2.76(3)\times10^{-4}$	0	–	–
$\zeta_t^{(z)}$	-0.3162 i)	-1.3078 i)	–	–
ϕ_{678} j)	31.054(4)			
$\lvert\zeta_{3,6a}^{(y)}\rvert$	0.570 k)			

a) Values are given in units of cm^{-1}, except for dimensionless $\zeta_t^{(z)}$ and $\zeta_{3,6a}^{(y)}$. The ground-state constants given in this table were used in the present analysis. b) Band origin $(\nu_0)_v$ includes a term $A(\zeta_t^{(z)})^2$. c) Standard deviations of the parameters given in parentheses apply to the last significant figure(s). d) $\alpha_3^A = -0.02$ cm^{-1} was assumed on the basis of the results for CH_3X molecules (Ref. 12). e) Ref. 13. f) The value does not involve the contribution of the Coriolis interaction between ν_6 and ν_3. g) Ref. 14. h) Ref. 15. i) Derived on the assumption $(A\zeta_t^{(z)})_v = A_v\zeta_t^{(z)}$. j) Mills' cubic force constant. k) Derived on the assumption $(B\zeta_{3,6a}^{(y)}) = (B_3B_6)^{\frac{1}{2}}\zeta_{3,6a}^{(y)}$.

errors due to the minor interactions which were not considered in the analysis. Table 2 shows the comparison of the present results with the previous ones,5,6) indicating that the precision of the parameters has been greatly improved owing to the higher spectral resolution and the more explicit analysis procedure utilized in the present study.

Table 2. Comparison of the parameters for ν_6, $\nu_7+\nu_8$, and ν_3 of CH_3CNa)

Parameter	Present work	Previous works	
		Matsuurab)	Duncan et al.c)
$(\nu_0)_6$d)	1448.007(8)e)	1448.42(7)	1448.03(10)
$(\nu_0)_{78}$d)	1410.605(9)	1410.74(10)	1410.2(2)
$(\nu_0)_3$	1381.78(16)	Not determined	1390(1)
α_6^A	0.04241(9)	0.046(1)	0.043(2)
α_{78}^A	-0.0209(6)	-0.033(7)	-0.058(15)
α_3^A	-0.02 (assumed)	Not determined	Not determined
α_6^B	-0.000262(10)f)	0	0
α_{78}^B	-0.000763(14)	0	0
α_3^B	-0.0005(2)f)	Not determined	Not determined
$\zeta_{6a,6b}^{(z)}$	-0.3162g)	-0.305	-0.303
$(\zeta_{78}^{(z)})_{eff}$	-1.3078g)	-1.285	-1.27
$\lvert\zeta_{3,6a}^{(y)}\rvert$	0.570h)	Not determined	0.55
ϕ_{678}	31.054(4)	31.14(12)	31.15(30)

a) See a) of Table 1. b) Ref. 5. c) Ref. 6. d) See b) of Table 1.
e) See c) of Table 1. f) See f) of Table 1. g) See i) of Table 1.
h) See k) of Table 1.

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