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Fermi Resonance Effects on the ν_1 Raman Bands of Liquid CH_2Br_2 and CH_3Br

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Synopsis. Applying Fermi-resonance-band-shape functions to the isotropic Raman band profiles of liquid CH_2Br_2 and CH_3Br in the ν_1 region, the peak frequencies, band-widths, and coupling constants of the ν_1 and combination vibrations have been determined.

In a previous paper on the Raman spectra of halogenated methanes in the liquid state,[1] Fukushi and Kimura have proposed the interpretation that the band around 2990 cm^{-1} of CH_2Br_2 is caused by Fermi resonance (FR) between the fundamental ν_1 and combination $2\nu_3+\nu_8+\nu_9$ vibrations. This interpretation was made on the basis of the fact that the band was observed in both the liquid[1] and solid[2] states as a doublet comprized of two components with comparable intensities. The band around 2960 cm^{-1} of liquid CH_3Br has an unsymmetric profile with a satellite on the high-frequency side.[1] The band was also considered to be a FR band between the ν_1 and $\nu_3+\nu_5+\nu_6$ vibrations, because its profile did not vary much with the temperature.[3] The decomposition of these bands into two components with the Voigt profile yielded the half-widths at half-height (hwhh) of 4.2 and 2.4 cm^{-1} for CH_2Br_2 and CH_3Br respectively.[4] These values are quite different from each other even though the bands belong to the same vibrational species. However, the Fermi-resonance band must be described by a linear combination of two Lorentzians and an unsymmetric function,[5] and the hwhh and peak frequency of each Lorentzian component are not equivalent to those of either the active or the passive band. Therefore, the hwhh values previously reported, especially for CH_2Br_2, may not be true, but only apparent. Thus, these bands have been reanalyzed using functions for the Fermi-resonance band shape (FRBS) proposed previously.[5]

Experimental and the Results of Band Analysis

The details of the experimental unit and technique have been published elsewhere.[1,3] The true power spectra were determined from the observed spectra by deconvoluting a slit function.

TABLE 1. RESULTS OF ANALYSIS FOR THE ν_1 ISOTROPIC RAMAN BANDS OF CH_2Br_2 AND CH_3Br(in cm^{-1} units)

	CH_2Br_2[a]		CH_3Br[a]	
	F[b]	L[c]	F[b]	L[c]
Ω^A	2988.0	2987.9	2956.1	2956.0
Ω^P	2989.3	2989.0	2963.5	2959.5
Γ^A	2.3	3.9	2.3	2.3
Γ^P	6.6	—	8.9	—
$\lvert\omega_\lambda\rvert$	6.2	4.6	4.1	2.1

a) Apparent peak frequencies: CH_2Br_2, 2983 and 2993 cm^{-1}; CH_3Br, 2955 cm^{-1}. b) Fermi-resonance-band shape (Figs. 1a and 2a). c) Two Lorentzians (Figs. 1b and 2b).

The band parameters of the two Lorentzian components; the hwhh, Γ_+ and Γ_-, the peak frequencies, Ω_+ and Ω_-, and the integrated intensities S_+ and S_-, are related to those for active (A) and passive (P) bands in the uncoupled state by these equations:[5]

$$\Gamma_\pm = \bar{\Gamma}_+/2 \pm (1/\sqrt{2})[(u^2+v^2)^{1/2}-v]^{1/2},$$

$$\Omega_\pm = \bar{\Omega}_+/2 \pm (1/\sqrt{2})[(u^2+v^2)^{1/2}+v]^{1/2},$$

$$S_\pm = (1/2) \pm [\bar{\Omega}_- u/2+\bar{\Gamma}_- v/2][u^2+v^2]^{-3/4},$$

where $\bar{\Gamma}_\pm=\Gamma^A\pm\Gamma^P$, $\bar{\Omega}_\pm=\Omega^A\pm\Omega^P$, $u=[\bar{\Omega}_-/2]^2-\bar{\Gamma}_-^2+|\omega_\lambda|^2$, and $v=2\bar{\Omega}-\bar{\Gamma}_-$, and where ω_λ is the coupling constant. The unsymmetric part is also expressed in terms of these parameters.[5] The parameter values were determined by the least-squares method applied to the band profiles. The true peak frequencies and band-widths for the active and passive modes and the coupling constants were calculated from the $\Gamma_\pm$, $\Omega_\pm$, and $S_\pm$ values thus obtained; they are listed in Table 1, Column F. Table 1, Column L, lists peak frequencies and band-widths obtained by analyzing the bands with two Lorentzians and the coupling constants estimated using equation usually quoted.[6] Figures 1 and 2 show the results of simulation for the ν_1 bands of CH_2Br_2 and CH_3Br at 290 K respectively, while (a) and (b) compare the results from the FRBS and Lorentz functions.

Discussion

As may be seen in Fig. 1, it is clear that the ν_1 band of CH_2Br_2 cannot be described as a superposition of two independent Lorentzians. The unsymmetric component of the FRBS makes a fairly large contribution to the whole band shape. The apparent band-widths, Ω_+ and Ω_- and the relative intensity of the two symmetric components, S_+ and S_-, shown in Figs. 1 (a) and (b) are not very different from each other, but the resulting band-widths, Γ^A, and coupling constants, $|\omega_\lambda|$, are quite different, as Table 1 shows.

For the ν_1 band of CH_3Br, both theoretical curves seem to reproduce the experiment, as is shown in Figs. 2 (a) and (b). On close examination, however, a difference between the two sets of results appears in the high-frequency region. In the results of analysis with the FRBS function, the unsymmetric component contributes significantly to the band profile and, as a result, the peak frequency of the satellite band, Ω^P, is high and the coupling constant, $|\omega_\lambda|$, is large compared with the results based on the two Lorentzians. The unperturbed frequency of the passive mode obtained by the FRBS analysis, 2963.5 cm^{-1}, is very close to the frequency of the combination band, $\nu_3+\nu_5+\nu_6$, calculated from the fundamental frequencies, 2965 cm^{-1}. As far as the Ω^A and Γ^A values are concerned, both analyses yielded the same results. The present results for CH_3Br are also coincident with the results obtained in the previous study,[3] where the band was

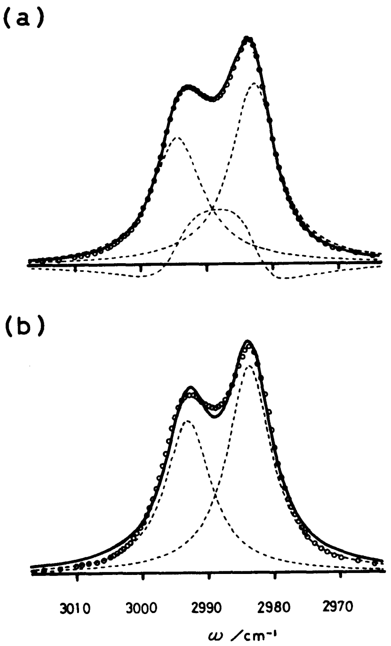

Fig. 1. Band simulation for the ν_1 isotropic Raman band of CH_2Br_2 with (a) Fermi resonance band shape function and (b) two Lorentzians; ○ observed, —— simulated curves, and ---- components.

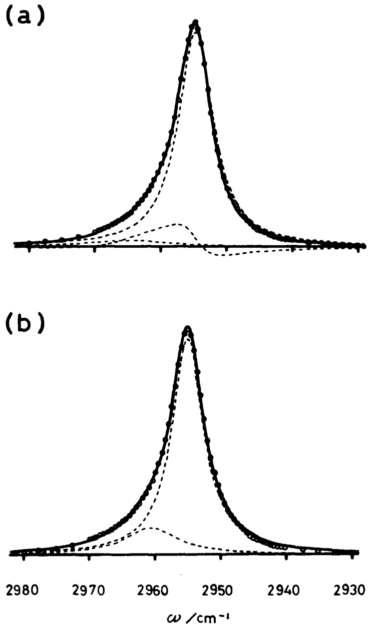

Fig. 2. Band simulation for the ν_1 isotropic Raman band of CH_3Br with (a) Fermi resonance band shape function and (b) two Lorentzians; ○ observed, —— simulated curves, and ---- components.

not deconvoluted and was analyzed with two Voigt functions. This indicates that the Fermi resonance effect on the band shape is insignificant for two bands with such a large separation and a weak coupling. The hwhh values of the ν_1 bands obtained for CH_2Br_2 and CH_3Br agree perfectly with each other. This suggests that the vibrational relaxation mechanisms of the ν_1 modes are similar to each other.

References

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6) Peak frequencies; $\omega=\bar{\Omega}_+\pm(\bar{\Omega}_-^2+|\omega_\lambda|^2)^{1/2}$ and $S_+/S_-=[(\bar{\Omega}_-^2+|\omega_\lambda|^2)^{1/2}+\bar{\Omega}_-]/[(\bar{\Omega}_-^2+|\omega_\lambda|^2)^{1/2}-\bar{\Omega}_-]$; G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Co., New York (1945), p. 215.