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The Polarization Measurement of He-Ne Laser Excitation Raman Lines of Liquid Acetone

Tsunetake Fujiyama and Takehiko Shimanouchi
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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Liquid acetone shows three Raman lines, near 530, 490, and 390 cm^{-1}, in the low-frequency region. These bands arise from the three deformation vibrations of the C–CO–C skeleton, namely, the CCC deformation (ν_8, a_1 species), the in-plane CO bending (ν_{18}, b_1 species), and the out-of-plane CO bending (ν_{23}, b_2 species). However, the assignments of these three lines have not yet been settled.[1] Some authors[2–4] assign ν_8 to the 490 cm^{-1} band, ν_{18}, to the 530 cm^{-1} band, and ν_{23} to the 390 cm^{-1} band, while others[5–7] reverse the assignments of ν_8 and ν_{23}.

Mikami-Abe[8] measured the infrared band envelopes of the 475, 409, and 320 cm^{-1} bands of acetone-d_6 in the gaseous state. The 409 cm^{-1} band shows the C-type envelope, which favors the second set of assignments. Alkins and Lippincott[9] measured the depolarization degree of Raman lines of liquid acetone using He–Ne laser excitation. The 490 cm^{-1} band was observed to be strongly polarized, thus supporting the first set of assignments.

Table 1. Depolarization ratios

Compound	$\Delta\nu$ (cm^{-1})	ρ (Ref. 9)	ρ (present results)
Acetone	394	0.76	0.774
	489	0.18	0.770
	531	0.80	0.792
	788	0.11	0.123
Chloroform	262	0.76	0.746
	366	0.11	0.114
	668	0.03	0.041
Methylene iodide	121	0.26	0.284
	485	0.10	0.092

Recently we measured the depolarization degree of the Raman lines of basic compounds and found that the observed value of the 490 cm^{-1} band of liquid acetone was considerably different from that observed by Alkins and Lippincott, although those of the other bands are in good agreement (Table 1). This finding obviates the idea that the 490 cm^{-1} line belongs to the a_1 species.

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Experimental

Acetone was purified by vacuum distillation, and its purity was checked by gas chromatography. The Raman spectra were recorded by means of a laser Raman spectrophotometer which had been constructed in our laboratory.[10] A Spex 1401 double monochromator was used as part of the equipment.

The polarized spectra were measured by the standard 90° scattering method, in which the polarization direction of the post-sample analyzer is fixed perpendicular to the direction of the monochromator slit. The pre-sample half-wave plate was used to rotate the direction of the polarization of the incident light. The exciting laser beam was passed only once through the cubic sample-cell, the edges of which were covered with sheets of black paper. The observation of the aperture was confined within an arc of 12 degrees. The polarization ratios were calculated from the relative band areas corresponding to the incident lights polarized parallel to and perpendicular to the polarization direction of the post-sample analyser.

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