BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3933—3935 (1970)

The Far-infrared Torsional Frequencies of Monohalogenoethanes

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(Received June 12, 1970)

In the case of the "one-top problem", it is known that intramolecular vibrations other than the torsion contribute quite little to the fine structure of the microwave spectrum.[1] Thus, we can obtain some information about the extent of interaction between the torsion and the other intramolecular vibrations by comparing the torsional frequencies observed in the infrared spectra with those obtained from the microwave splitting through the calculation by using the P.A.M.[2] (principal-axes method) or the I.A.M.[2] (internal-axis method).

The far-infrared spectra were recorded on a Hitachi FIS-1 vacuum, grating, double-beam spectrophotometer. All the monohalogenoethanes used were obtained from commercial sources; they were purified by vapor-phase chromatography and then dried with phosphorus pentoxide. Considerable precautions were taken to remove the residual water. The vapor of monohalogenoethane was introduced into a gas-cell which had been especially built for the instrument. Its path length is veriable in increment of 1.2 m up to 6 m. In order to avoid interference, wedged polyethylene sheets were used as the cell windows.

The observed torsional frequencies are given in Table 1, together with those values calculated from the microwave splitting data.[2,3] The torsional frequencies for ethyl fluoride and ethyl chloride have been reported by Sage and Klemperer[4] and Fateley and Miller[5] respectively. We observed not only those frequencies, but also the 3E→4E transition bands for these molecules (see Fig. 1). It is of some interest to note the splitting of the A and E levels for higher vibrational states, as is expected from the theory.[2,3] Such splitting has not previously been observed.[4-6] Although the reason for this is not clear, it may be remembered that the previous data were obtained

TABLE 1. CALCULATED (FROM MICROWAVE DATA) AND OBSERVED INFRARED TORSIONAL FREQUENCIES FOR MONOHALOGENOETHANES

v-v'		C_2H_5F MW[a] (cm^{-1})	C_2H_5F IR (cm^{-1})	C_2H_5Cl MW[b] (cm^{-1})	C_2H_5Cl IR (cm^{-1})	C_2H_5Br MW[c] (cm^{-1})	C_2H_5Br IR (cm^{-1})	C_2H_5I MW[d] (cm^{-1})	C_2H_5I IR (cm^{-1})
0—1	A	244	243.5	250.8	250.8	247.2	247.8	228	237.0
	B	244		250.8		247.2		228	
1—2	E	227	226.5	235.0	235.0	231.8	232.8	213	221.0
	A	227		235.0		231.8		213	
2—3	A	208	209.0	217.3	218.0	214.7	216.4	196	
	E	207		216.9		214.4		195	
3—4	E	186	189.6	197.0	199.5	195.2	194.0	176	
	A	176	178.4	192.8	196.1	191.8	(191.2)	170	
V_3(cal/mol)		3330±100[a]		3685±12[b]		3684±10[c]		3220±100[d]	
S		80.0[a]		94.43[b]		97.4[c]		87.1[d]	

a) D. R. Herschbach, *J. Chem. Phys.*, **25**, 358 (1956).
b) R. H. Schwendeman, *ibid.*, **36**, 1245 (1962).
c) C. Flanagan and L. Pierce, *ibid.*, **38**, 2963 (1962).
d) T. Kasuya, *J. Phys. Soc. Jap.* **15**, 1273 (1960).

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[3] D. R. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959).

[4] G. Sage and W. Klemperer, *ibid.*, **39**, 371 (1963).

[5] W. C. Fateley and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963).

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with a single-beam spectrometer. The infrared torsional frequencies for gaseous ethyl bromide and ethyl iodide are observed for the first time in the present study (Fig. 2). In the case of ethyl iodide, the agreement between the infrared frequencies and those obtained from the microwave splitting data is not so good. This is probably due to experimental error in the microwave measurements; Kasuya[7] has reported that his microwave datum for ethyl iodide will be refined in the future.

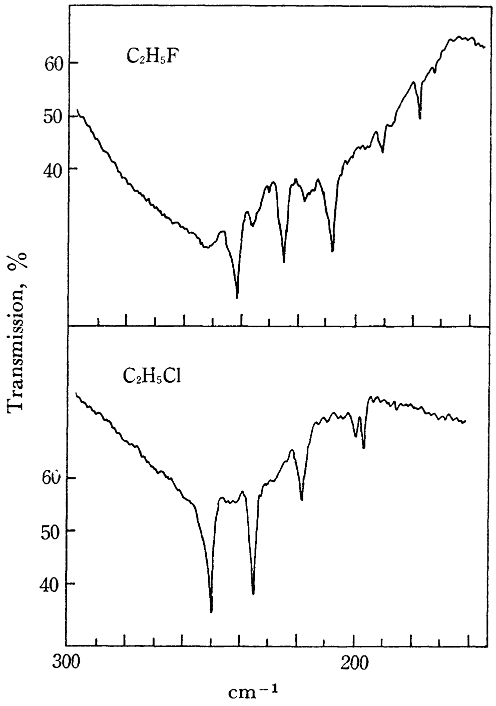

Fig. 1. Far-infrared spectra of ethyl fluoride and ethyl chloride.
(Path length: 4.8 m,
Pressure: Saturated vapor pressure at room temperature)

The 201 cm^{-1} band of the gaseous ethyl iodide in Fig. 2 was identified as the difference band between two fundamentals, 947 cm^{-1} (A′) and 741 cm^{-1} (A″), despite the fact that it was stronger than the torsion bands. This assignment is based on the following reasons: (1) In the liquid spectrum, the corresponding band was observed at 204 cm^{-1}, and its envelope was rather sharper than that in the gas (Fig. 3). However, a torsion band is usually weaker and broader in the liquid than in the gas phase. (2) If the torsional frequencies were 201 cm^{-1}, the barrier height, V_3, would be calculated to 2590 cal/mol. This is curiously low, since the value in ethane is 3000

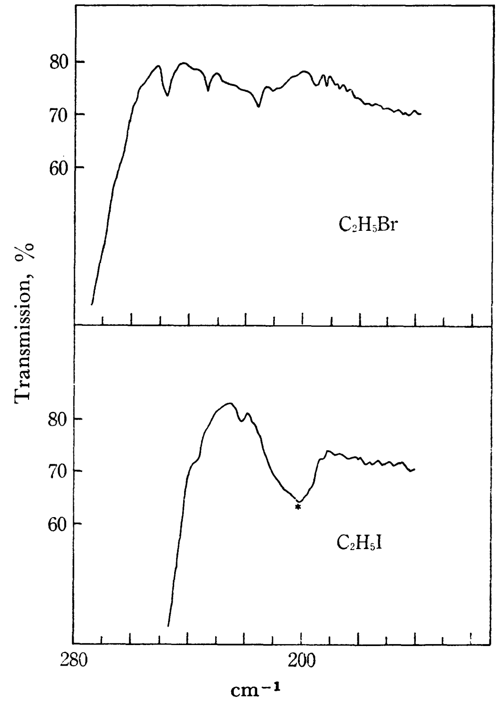

Fig. 2. Far-infrared spectra of ethyl bromide and ethyl iodide.
(Path length: 1.0 m for ethyl bromide,
3.6 m for ethyl iodide.
Pressure: Saturated vapor pressure at room temperature, for the both)
* This band was identified as a difference band.

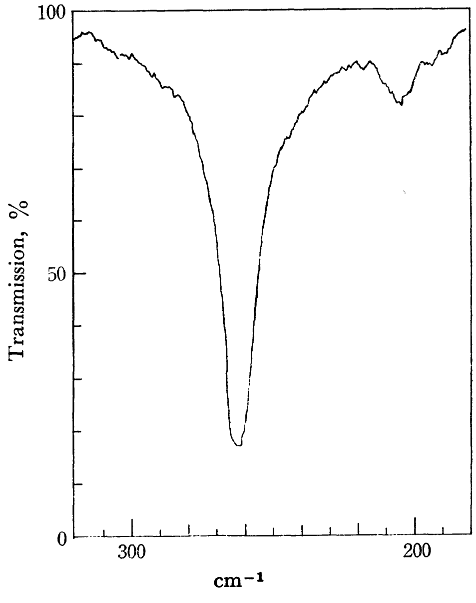

Fig. 3. Far-infrared spectra of liquid ethyl iodide.
Path length: 0.3 mm; The 262 cm^{-1} band is an A' fundamental, associated with CCI bending.

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7) T. Kasuya, *J. Phys. Soc. Jap.*, **15**, 1273 (1960).

cal/mol.[8] (3) The band remained constant in intensity and frequency in the course of time. No rotation bands of hydrogen iodide were observed, either. Therefore, the band is not due to any decomposition product. (4) The combination band of the fundamentals appeared at 1709 cm^{-1}. The difference between the calculated and observed frequencies, 21 cm^{-1}, seems to be a little large. This is because the 1709 cm^{-1} band is very broad (the half band-width, 120 cm^{-1}) and consists of two combination bands, corresponding to 1712 (1210 A′ + 502 A″) and 1688 cm^{-1} (947 A′ + 741 A″).[9]

Except for the case of ethyl iodide, the agreement between the infrared frequencies and those obtained from the microwave splitting data is excellent. This suggests that the coupling of the CH_3 torsional vibration with the other intramolecular vibrations is quite small. This, in turn, justifies the treatment for obtaining the potential barrier to internal rotation from the infrared torsional frequency.[4–6] This is further supported by the fact that the potential energy distributions for the tosional vibration in the trans configuration of 1,2-dichloro-[10,11] and 1,2-dibromoethane[12] are 90 and 80% respectively.

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