LETTERS TO THE EDITORS

Microwave Spectrum of Methyl Chloride in Excited Vibrational States

The rotational spectra of methyl halides in the vibrational ground state have been the subject of several investigations (*1*). Only a few transitions in excited vibrational states of CH_3Cl, CH_3Br, and CH_3J have been reported (*2, 3*). In the present investigation a systematic search was made for microwave transitions of CH_3Cl in the frequency region between 26 and 27 GHz.

The microwave spectrometer of well-known design (*4*) was equipped with 2 kHz square-wave Stark modulation and bolometer detection. The ultimate sensitivity (smallest detectable absorption coefficient) was 4×10^{-10}cm^{-1} with a time constant of 10 seconds. The assignment of observed absorption lines was based on the hyperfine structure due to the quadrupole moment of the chloride nucleus and on the comparison of measured and calculated absorption coefficients (*5, 6*). Frequencies were measured with a secondary frequency standard (General Radio 1112 A and B) and an interpolation receiver. The electric dipole moment was determined from the Stark splitting pattern of the transitions by using a Stark cavity as an absorption cell (*6*).

TABLE I

FREQUENCIES AND INTENSITIES OF $J = 0 \rightarrow 1$ TRANSITIONS OF $CH_3{}^{35}Cl$ IN EXCITED VIBRATIONAL STATES

Vibrational state	Transition		Frequency[a] (MHz)	Absorption coeff. (cm^{-1})	
	F_i	F_f		Observed	Calculated
$v = 0$	3/2	5/2	26 589.48	$(8.0 \pm 0.2) \times 10^{-6}$	8.1×10^{-6}
	3/2	3/2	26 570.80	$(5.5 \pm 0.1) \times 10^{-6}$	5.4×10^{-6}
	3/2	1/2	26 604.42	$(2.9 \pm 0.1) \times 10^{-6}$	2.7×10^{-6}
$v_2 = 1$	3/2	5/2	26 344.00		1.2×10^{-8}
	3/2	3/2	26 325.38	$(8.3 \pm 0.3) \times 10^{-9}$	7.9×10^{-9}
$v_3 = 1$	3/2	5/2	26 359.00	$(2.2 \pm 0.1) \times 10^{-7}$	2.4×10^{-7}
	3/2	3/2	26 340.27	$(1.5 \pm 0.1) \times 10^{-7}$	1.6×10^{-7}
	3/2	1/2	26 373.96	$(7.5 \pm 0.5) \times 10^{-8}$	8.0×10^{-8}
$v_5 = 1$	3/2	5/2	26 684.40	$(6.8 \pm 0.3) \times 10^{-9}$	7.4×10^{-9}
	3/2	3/2	26 665.55	$(4.7 \pm 0.3) \times 10^{-9}$	4.9×10^{-9}
	3/2	1/2	26 699.32	$(2.2 \pm 0.3) \times 10^{-9}$	2.5×10^{-9}
$v_6 = 1$	3/2	5/2	26 491.49	$(5.8 \pm 0.1) \times 10^{-8}$	6.0×10^{-8}
	3/2	3/2	26 472.79	$(3.5 \pm 0.1) \times 10^{-8}$	4.0×10^{-8}
	3/2	1/2	26 506.50	$(1.9 \pm 0.1) \times 10^{-8}$	2.0×10^{-8}

[a] Measured frequencies are accurate to 0.05 MHz.

TABLE II

SOME MOLECULAR CONSTANTS OF $CH_3{}^{35}Cl$ IN EXCITED VIBRATIONAL STATES

Vibrational state	B_v (MHz)	α (MHz)	$-eqQ$ (MHz)	μ (Debye)
$v = 0$	13 292.87 ± 0.02		74.71 ± 0.1	1.892 ± 0.001
$v_2 = 1$	13 170.14 ± 0.02	122.73 ± 0.03	74.51 ± 0.1	
$v_3 = 1$	13 177.63 ± 0.02	115.24 ± 0.03	74.87 ± 0.1	1.923 ± 0.002
$v_5 = 1$	13 340.32 ± 0.02	−47.45 ± 0.03	75.05 ± 0.3	
$v_6 = 1$	13 243.87 ± 0.02	49.00 ± 0.03	74.90 ± 0.1	1.897 ± 0.004

Table I shows the frequencies and absorption coefficients of assigned transitions. Only transitions in excited states of v_1 and v_4 are missing because they were too weak to be observed. The measured frequencies for $v_3 = 1$ and $v_6 = 1$ are in good agreement with the values reported by Kraitchman *et al.* (*2*). Table II shows the rotational constants B_v, the rotation-vibration constants α_v, the quadrupole coupling constants eqQ, and the electric dipole moments μ for excited vibrational states. It is interesting to note the relatively large negative value of α_5 in contrast to the corresponding positive value for CH_3J (*3*). The eqQ values in the excited vibrational states do not differ much from the ground state value, in accordance with measurements on CH_3J. The electric dipole moment is about 1% larger than the value reported by Shulman *et al.* (*7*).

Measurement of the top-intensity α_{max} of the ground state transition as a function of temperature showed that α_{max} is proportional to $T^{-2.5}$. Thus it can be concluded that the line-width constant $\Delta\nu/p$ is proportional to T^{-1}. This is a strong indication that the collisions contributing to the line-width are primarily due to dipole-dipole interactions.

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" and was made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.).

REFERENCES

1. Landolt-Bornstein Tables, New Series, Group II. "Molecular Constants from Microwave Spectroscopy Measurements," Vol. 4, Springer Verlag, Berlin (1967).
2. J. KRAITCHMAN AND B. P. DAILEY, *J. Chem. Phys.* **22,** 1477 (1954).
3. Y. MORINO AND C. HIROSE, *J. Mol. Spectry.* **22,** 99 (1967).
4. R. H. HUGHES AND E. B. WILSON, *Phys. Rev.* **71,** 562L (1947).
5. A. DYMANUS, *Physica* **25,** 859 (1959).
6. H. A. DIJKERMAN, Thesis, Univ. of Utrecht, The Netherlands (1966).
7. R. G. SHULMAN, B. P. DAILEY, AND C. H. TOWNES, *Phys. Rev.* **78,** 145 (1950).

Physics Laboratory
State University of Utrecht
The Netherlands
Received July 27, 1967

J. P. DE JONGH
H. A. DIJKERMAN

The Ultraviolet Absorption Spectra of the Oxalyl Halides

The oxalyl halides (COX)(COY), where X and Y are either the same or different halogen atoms, are a group of closely-related molecules whose spectral analyses enable useful comparisons to be made. The vibrational spectra of some of these molecules have recently been