

CHROM. 11,973

GAS CHROMATOGRAPHIC DETECTION OF ORGANOGermanium COMPOUNDS BY SURFACE OR GAS-PHASE LUMINESCENCE

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SUMMARY

The flame photometric detector responds to organic compounds of germanium similar to the way in which it responds to organotins. Two modes of operation have been investigated; these are based on luminescence originating on a quartz surface (emitter unknown) or in the gas phase (GeH bands).

The surface luminescence is the more sensitive analytical mode: 1 pg of tetrabutylgermanium can be detected, corresponding to *ca.* $1 \cdot 10^{-14}$ g Ge/sec. However, peaks may be broadened by the surface effect, and tin responds significantly stronger than germanium.

The gas-phase luminescence, monitored at 650 nm, is the less sensitive mode: 15 pg of Bu₄Ge can be detected, corresponding to *ca.* $2 \cdot 10^{-13}$ g Ge/sec. However, peaks are not broadened, and germanium is favored over phosphorus, tin, sulfur, and hydrocarbon by approximately 1, 2, 1-3, and 6 orders of magnitude, respectively.

INTRODUCTION

In its discovery and chemical importance, germanium has been relegated to a wallflower existence between its more prominent sister elements silicon and tin. As Glockling¹ expressed it in his book on the chemistry of germanium: "Early studies established that its properties seemed to fit so clearly between those of silicon and tin, that its chemistry appeared to lack novelty. . . What can be done with germanium can almost certainly be achieved more cheaply with silicon or tin analogues".

In analytical chemistry, too, germanium is generally associated with silicon and/or tin methodology.

Spectroscopic approaches have frequently been used for inorganic germanium determination. For instance, Gilbert² found 5 mg Ge/l to be the detection limit for an air-hydrogen flame doped with isopropanol. Recently, germane has been detected by "metastable transfer emission spectroscopy" at the 0.1 ppb* level in the gas phase³.

GeH₄ is, of course, easily generated by the conventional hydride technique,

* Throughout this article, the American billion (10⁹) is meant.

and so are germanes in varying states of organic substitution. It comes as little surprise, therefore, that gas chromatography (GC) has often served to separate germanium hydrides from other volatile sample constituents or derivatives⁴⁻⁶.

Besides general GC detectors such as thermal conductivity or flame ionization detectors (FID), a variety of selective detection modes have been explored. Hill and Aue⁷ found 0.6 ng to be the minimum detectable amount of tetrabutylgermanium in a hydrogen-atmosphere flame ionization detector (HAFID). Mass spectrometric approaches by Lussi-Schlatter and Brandenberger⁸ and Kadeg and Christian⁹ led to germane detection limits of 10 pg and 1 ppb, respectively. Recently, Braman and Tompkins¹⁰ quoted 0.4 ng Ge for atomic emission from a d.c. discharge. Robbins *et al.*¹¹, using a microwave-induced plasma emission detector with hydride generation and condensation facilities, detected 3 ng (0.15 ppb) of germanium.

We had been interested for some time to analyze for organometallics by GC with a flame photometric detector (FPD) *via* a variety of band emissions. Germanium's congener tin proved to be especially interesting in this context: Three of its spectral features (closely paralleled by their germanium analogues) were analytically useful.

First, and of most appeal to spectroscopists, the sharp SnH bands. These were detected by Dagnall *et al.*¹² in a cool hydrogen-air diffusion flame down to a minimum detectable limit of 1.5 ppm. In a typical FPD, about 0.1 ng of tetrapropyltin could be seen *via* this red emission¹³. For an FPD of their own construction, Braman and Tompkins¹⁴ recently reported detection limits for stannane and methylstannanes corresponding to approximately 0.01 ng Sn. Further improvement appears possible; for instance, Kapila¹⁵ detected 0.5 pg tetrabutyltin with a lab-made FPD.

The second spectral feature of molecular tin emission is a greyish continuum peaking at 485 nm. It has been ascribed¹² to SnO. Our group has used it in a dual-channel (emission-cum-ionization) detector made by attaching a grating spectrometer to a regular FID. Linear responses were found from 10 to 10⁴ ng of various organotins¹⁶.

The third, most sensitive, and potentially most interesting feature of tin luminescence is a broad emission ranging from approximately 350 to 500 nm, peaking at 390 nm. It occurs at the surface of (clean) quartz. The minimum detectable amount of tetrapropyltin in this mode¹³ was 0.2 pg; it has since been lowered¹⁷ to 40 fg or *ca.* 5 · 10⁻¹⁶ g Sn/sec.

Based on these experiences with tin we decided to investigate the flame photometric detection of a germanium compound in two modes: *via* its luminescence on a quartz surface and *via* its GeH (ref. 18) luminescence in the gas phase.

EXPERIMENTAL

A Shimadzu dual-channel FPD was used atop at GC-4BM gas chromatograph made by the same company. Typical experimental parameters are given in Table I for the two operational modes monitoring "surface" and "gas-phase" emissions. The "bisected" quartz tube was a large tube of the same dimensions as the regular Shimadzu FPD quartz chimney, but bisected (horizontally traversed) by a central quartz tube of *ca.* 4 mm diameter. The position of this tube above the flame is schematically

TABLE I
TYPICAL DETECTOR CONDITIONS

	Mode	
	"Surface"	"Gas-phase"
Hydrogen flow-rate, ml/min	240	100
Air flow-rate, ml/min	60	40
Nitrogen flow-rate (from column), ml/min	30	30
Optical filter	none	650 nm interference or 600 nm cut-off (long pass) (or monochromator)
PM tube (Hamamatsu)	R-268	R-1104
Quartz tube	"bisected"	regular Shimadzu chimney

shown in the insert of Fig. 2. It was "cleaned" by microliter injections of Freon 113 while keeping the flame lit.

GC separations were done (for "surface" experiments) on 5% Carbowax 20M on Chromosorb W, 45-60 mesh, and (for "gas-phase" experiments) on bonded Carbowax 20M on Chromosorb W, 80-100 mesh¹⁹. Both phases were packed into 50 × 0.3 cm I.D. borosilicate columns.

To take "spectra", a Jarrel-Ash 0.25 m grating monochromator was mounted as one optical channel. The other channel was left intact and operated in a non-dispersive FPD mode. This was done to be aware of, and allow correction for, any possible changes in detector sensitivity, injection size, etc.

RESULTS AND DISCUSSION

Fig. 1 shows the spectral features obtained from injections of tetra-*n*-butylgermanium. The most sensitive one is the blue glow on the surface of the horizontal

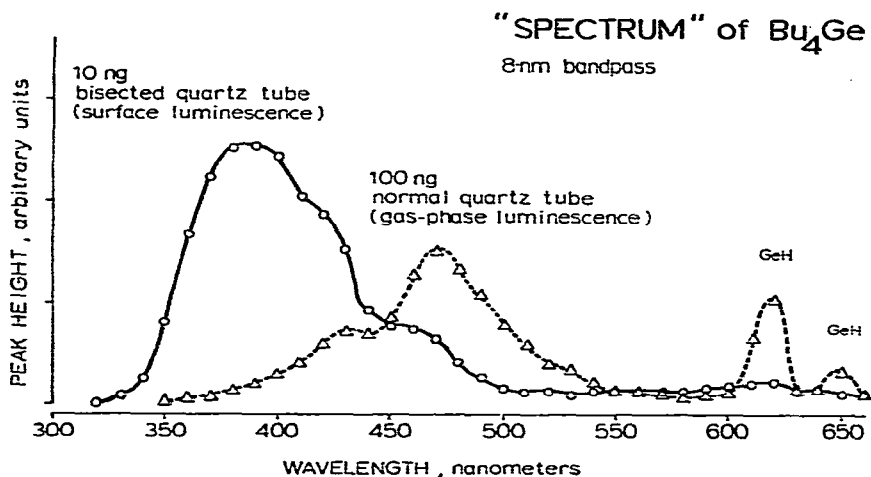


Fig. 1. Peak heights of tetra-*n*-butylgermanium injections at different wavelengths. R-268 PM tube. O, 10-ng injections, Freon-cleaned bisected quartz tube (no mask). Flow-rates and column as given in Table I under "Surface", except 40 ml/min hydrogen flow. Δ , 100-ng injections, regular quartz chimney. Flow-rates and column as given in Table I under "Surface", except 80 ml/min hydrogen flow.

quartz tube above the flame. Ten times more Bu_4Ge was needed to monitor the gas-phase emission from a regular Shimadzu quartz chimney without bisecting tube—a greyish diffuse glow above a central red core.

The latter, the well-known GeH bands¹⁸, can be further resolved by using a 2-nm bandpass. The broad emissions centered around 390 and 470 nm, however, remained featureless under these conditions.

The greyish gas-phase emission around 470 nm may be due to GeO , in analogy to the very similar luminescence given by tin compounds and attributed by Dagnall *et al.*¹² to SnO . A well-resolved GeO spectrum was obtained (under very different conditions) and interpreted by Tewari and Mohan²⁰. Its strongest band lies at 4779.4 Å. For our purpose, the greyish FPD emission was of little interest since it is (a) subject to interference by the analogous Sn feature and (b) less sensitive than the surface glow.

The origin of the blue surface glow of germanium is unknown. It is very similar, though not identical, to that of tin.

That there truly exists a surface-dependent emission is obvious from visual observation. It can also be demonstrated in a quantitative manner if one FPD channel is made to monitor the gas phase, the other one the tube surface. Fig. 2 shows a schematic of the bisected quartz tube used for this purpose: masks have been painted on in china ink. The results are expressed in this graph as the response ratios of the two channels, and germanium is compared to tin and sulfur—the latter two representing surface-active and gas-phase-active species, respectively. They are separated by two to three orders of magnitude even in this rather crude experimental design. Obviously, this effect could be exploited for differentiation between the two types of elements.

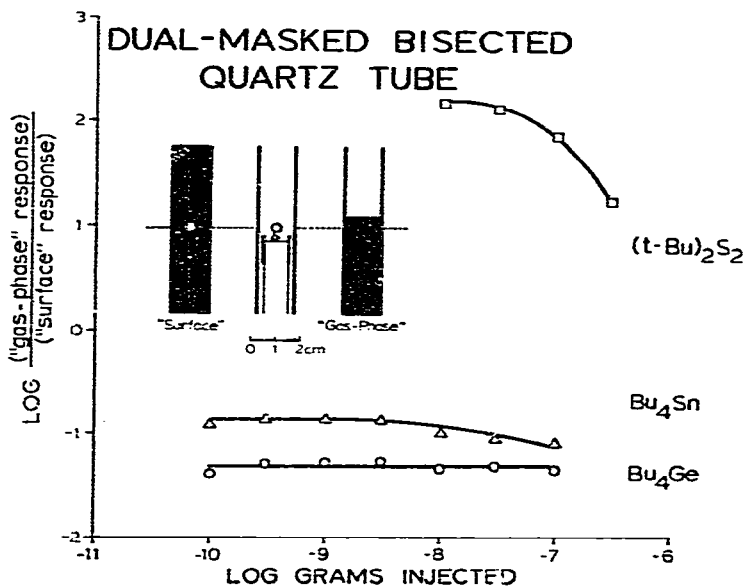


Fig. 2. Ratio of "gas-phase" vs. "surface" emissions measured through china ink-painted masks on bisected quartz tube as indicated. Center drawing (without mask) for comparison only. Conditions as given under "Surface" in Table I.

Surface luminescence being the most sensitive emission mode for Bu_4Ge suggested that calibration curves be established. The results, together with those for tin, sulfur and carbon compounds run under the same conditions, are shown in Fig. 3.

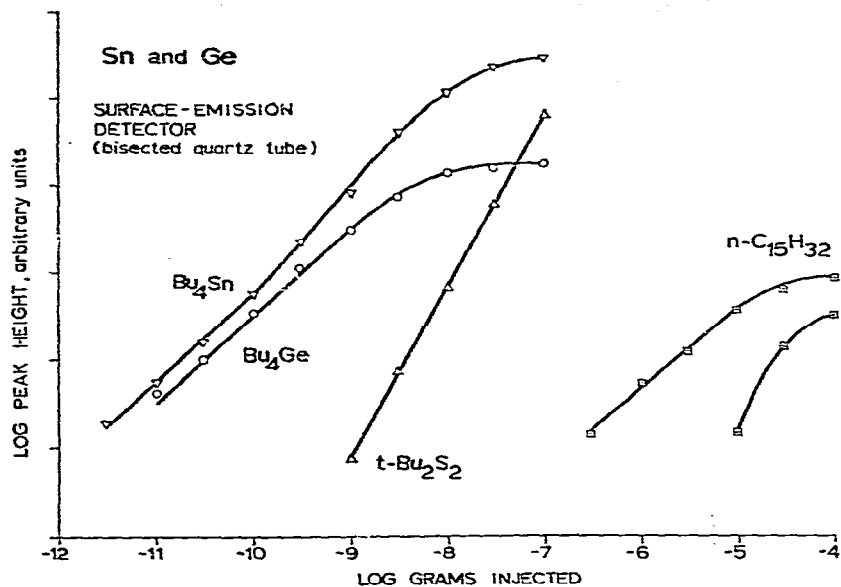


Fig. 3. Calibration curves for compounds as indicated. Conditions as given under "Surface" in Table I.

The carbon compound, $n\text{-C}_{15}\text{H}_{32}$, produces both positive (normal) and negative (inverted) peaks, as indicated by the data points. The selectivity of tetra-butylgermane vs. pentadecane exceeds four orders of magnitude. However, tetra-butylstannane responds still stronger. As expected from its S_2 emission spectrum with the strongest peak at 394 nm, sulfur is also an important interferent (this interference could be significantly suppressed by using a mask that discriminates against gas-phase emissions).

In a separate experiment, aided by an active electronic filter, the minimum detectable amount of Bu_4Ge was determined as 1.3 pg or $0.8 \cdot 10^{-14}$ g Ge/sec. However, the peak was clearly broadened by the surface effect. The extent of broadening (mainly tailing) depended on conditions and immediate history of the detector. It was more severe than the analogous effect produced by tin compounds. It is interesting in this context that Tewari and Mohan²⁰, in an aside on experimental difficulties encountered with germanium compounds, state that "the vapors of hot GeO_2 . . . sharply react with quartz".

No such peak broadening was expected from the gas-phase luminescences and none was observed. Of the two, the GeH emission appeared the better candidate for analytical utilization: the sharper hydride bands promised improved selectivity vs. the most likely interference, that from germanium's congener tin.

The optimization of flow-rates for GeH was routine, and is shown in Fig. 4.

"GeH" EMISSION

(above 600 nm)

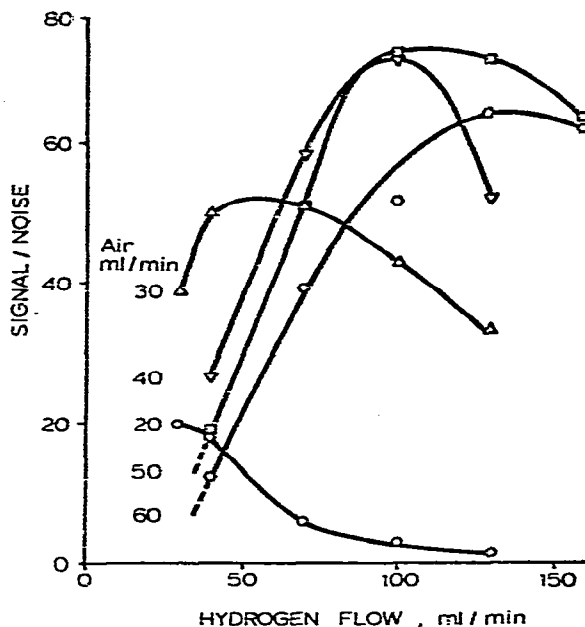


Fig. 4. Tetra-*n*-butylgermanium response profiles for various air and hydrogen flows. Conditions as given under "Gas-phase" in Table I. Cut-off filter 600 nm.

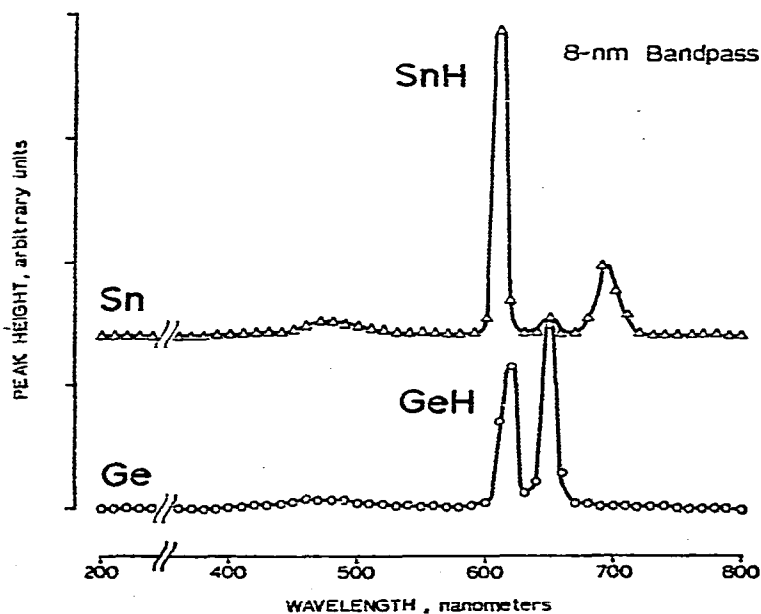


Fig. 5. Peak heights for injections of tetrabutyl derivatives of tin and germanium at different wavelengths. 8-nm bandpass monochromator. Hydrogen flow-rate, 70 ml/min. Other conditions as given under "Gas-phase" in Table I.

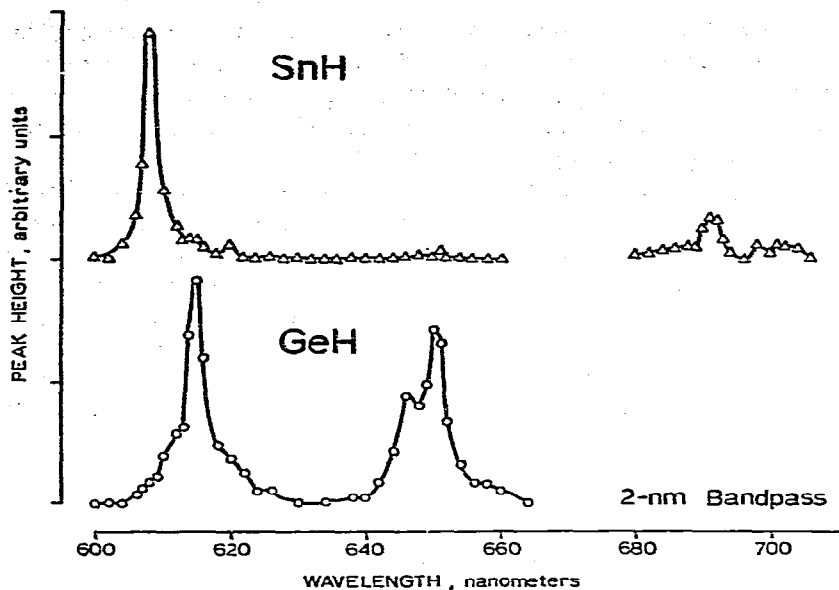


Fig. 6. Same as Fig. 5, but 2-nm bandpass and 100 ml/min hydrogen flow.

Then, using these optimized conditions, the "spectrum" of tetra-*n*-butylgermanium was run contrasted with that of its tin analogue. Fig. 5 shows the spectra as observed through an 8-nm bandpass. Note that the oxide (?) emissions are now hardly noticeable.

A 2-nm bandpass run, shown in Fig. 6, then aided in the choice of an interference filter for regular FPD operation. Although the GeH band at 650 nm

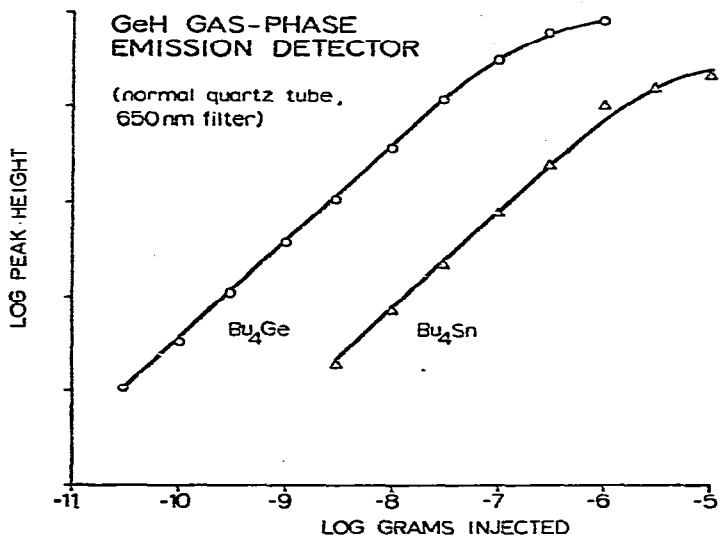


Fig. 7. Calibration curves for tetrabutyl derivatives of germanium and tin. 650 nm interference filter. Conditions as given under "Gas-phase" in Table I.

coincides with a minor band in the Sn spectrum, it was considered the first choice.

Hence, calibration curves were run with a 650 nm interference filter and at conditions optimized for Ge. These curves are shown in Fig. 7. Now Bu_4Ge responds stronger than Bu_4Sn by almost two orders of magnitude. The linear range exceeds 10^3 (the linear parts are drawn with a slope of exactly one).

Spot-checks with potentially interfering species showed that phosphorus responds unexpectedly strong at 650 nm: Diphenylmethylphosphine was only a factor of 17 less sensitive than tetrabutylgermanium. Sulfur response is quadratic—the long row of S_2 bands diminishes only slowly towards longer wavelengths—and Ge/S selectivity hence varies, between one and three orders of magnitude. Hydrocarbons hardly respond at all; the germanium compound was a millionfold more sensitive.

The minimum detectable amount of Bu_4Ge in the GeH mode was 15 pg, corresponding to $2 \cdot 10^{-13}$ g Ge/sec. This could be further improved and likely will be. Such improvement, however, is beyond our present intentions.

ACKNOWLEDGEMENTS

Thanks are due to Jürgen Müller for making the bisected quartz tube, and to Bob Moseman for a sample of his speedy-synthesis version of bonded Carbowax 20M¹⁹. This research was supported by NRC grant 9604.

REFERENCES

- 1 F. Glockling, *The Chemistry of Germanium*, Academic Press, London, New York, 1969.
- 2 P. T. Gilbert, in *Chemiluminescent Flame Spectroscopy, Proc. 10th Colloquium Spectroscopium Internationale*, 1963, pp. 175–215.
- 3 D. G. Sutton, J. E. Melzer and G. A. Capelle, *Anal. Chem.*, 50 (1978) 1247.
- 4 G. Guiochon and C. Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Sci. Publ., Ann Arbor, Mich., 1973.
- 5 C. S. G. Phillips and P. L. Timms, *Anal. Chem.*, 35 (1963) 505.
- 6 A. D. Zorin, G. G. Devyatykh, V. Ya. Dudorov and A. M. Amel'chenko, *Russ. J. Inorg. Chem.*, 9 (1964) 1364.
- 7 H. H. Hill, Jr. and W. A. Aue, *J. Chromatogr.*, 122 (1976) 515.
- 8 B. Lussi-Schlatter and H. Brandenberger, *Advances in Mass Spectrometry in Biochemistry and Medicine*, Vol. 2, Spectrum Publications, 1976.
- 9 R. D. Kadeg and G. D. Christian, *Anal. Chim. Acta*, 88 (1977) 117.
- 10 R. S. Braman and M. A. Tompkins, *Anal. Chem.*, 50 (1978) 1088.
- 11 W. B. Robbins, J. A. Caruso and F. L. Fricke, *Analyst (London)*, 104 (1979) 35.
- 12 R. M. Dagnall, K. C. Thompson and T. S. West, *Analyst (London)*, 93 (1968) 518.
- 13 W. A. Aue and C. G. Flinn, *J. Chromatogr.*, 142 (1977) 145.
- 14 R. S. Braman and M. A. Tompkins, *Anal. Chem.*, 51 (1979) 12.
- 15 S. Kapila, personal communication.
- 16 W. A. Aue and H. H. Hill, Jr., *J. Chromatogr.*, 70 (1972) 158.
- 17 C. G. Flinn and W. A. Aue, unpublished results.
- 18 R. W. B. Pearce and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, London, 1963, p. 167.
- 19 R. F. Moseman, *J. Chromatogr.*, 166 (1978) 397.
- 20 D. P. Tewari and H. Mohan, *J. Mol. Spectrosc.*, 39 (1971) 290.