Vibrational Assignments and Intramolecular Force Field of Trimethylaluminum*

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Trimethylaluminum is the simplest member of the trialkylaluminum series, all of which are important components of the Ziegler-type catalyst. Accordingly, this compound has been extensively investigated, although its reactivity is low in olefin polymerization. The reaction and the structure of trimethylaluminum-diphenylamine complex have been reported on previously.(1)

Trimethylaluminum has been found to be in a bridged structure by an X-ray diffraction method.(2) The vibrational spectra and their assignments have been studied by several authors.(3-10) Onishi et al.(7,9) have measured the infrared spectra in the region 700—280 cm^{-1} and have calculated the normal vibrations on the basis of a modified Urey-Bradley field. Ogawa et al.(6,10) have measured the far infrared

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1) M. Kawai, T. Ogawa and K. Hirota, This Bulletin, **37**, 1302 (1964).

2) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

3) G. P. van der Kelen and M. A. Herman, *Bull. soc. chim. Belges.*, **65**, 362 (1956).

4) E. G. Hoffmann, *Z. Electrochem.*, **64**, 616 (1960).

5) K. Hirota, K. Kuwata and T. Imanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 1302 (1962).

6) T. Ogawa, K. Hirota, T. Imanaka, K. Fukushima and T. Miyazawa, "Proceedings of the International Symposium on Molecular Structure and Spectroscopy," Science Council of Japan, Tokyo (1962), A309.

7) T. Onishi, I. Nakagawa and T. Shimanouchi, ibid., (1962), A310.

8) A. P. Gray, *Can. J. Chem.*, **41**, 1511 (1963).

9) T. Onishi and T. Shimanouchi, *Spectrochim. Acta*, **20**, 325 (1964).

10) T. Ogawa, K. Hirota and K. Fukushima, This Bulletin, **37**, 1243 (1964).

spectra in the region 700—65 cm^{-1} and have calculated the normal vibrations by the use of the Urey-Bradley potential function as supplemented with a few correction terms. In the present study the treatment of the normal vibrations was refined, and the vibrational spectra were reassigned.

The standard errors of potential constants may be used in discussing the reliability of a potential field and in studying the transferability of the potential terms. The uncertainties in potential constants arise not only from experimental errors, but also from deficiencies in the physical model of the potential field. The standard errors which are due to the latter source have previously been discussed, and a general formula has been derived.[11] This formula was used, in the present study, for the calculation of the standard errors of the potential constants of trimethylaluminum.

Experimental

In studying the reaction mechanism, it is interesting to measure the infrared spectra of reactive substances or intermediate species. Since unstable organic samples react with or dissolve a vacuum grease, it was not practical to construct a vacuum liquid cell with alkali halide crystals. Therefore, a new device was worked out for the infrared measurement of extremely reactive substances.

This cell was made of polyethylene and could be kept in a vacuum of about 10^{-2} mmHg for a few days. The margin of polyethylene films, 10 cm. × 8 cm. × 0.5 mm., was heated and pressed by a brass press in order to form an envelope; a glass tube 4 mm. in diameter had been inserted between the films in advance. Polyethylene films were readily melted and adhered to each other and to the glass tube. The cells thus constructed are satisfactorily airtight. In addition, vacuum resin was spread all over the outer surface of the cell, except for the optical path, in order to ensure the vacuum and to prevent the cell from accidentally breaking. The liquid sample was distilled in a side arm near the cell and poured through the glass tube into the cell in a vacuum. When it was necessary to increase the sample thickness, nitrogen gas was introduced in order to help more liquid squeeze into the cell. With this cell, the infrared spectra could be measured in the 4000—3100 cm^{-1}, 2500—1500 cm^{-1}, 1250—750 cm^{-1}, and below 700 cm^{-1} regions.

Normal Vibration Treatment

The molecular structure of trimethylaluminum (Fig. 1) belongs to the point group D_{2h}, and the geometrical parameters are $a=1.99\,\text{Å}$, $b=2.24\,\text{Å}$, $l=2.57\,\text{Å}$, $\angle\alpha=124°$ and $\angle\beta=110°$.[2] This structure of trimethylaluminum is quite similar to that of diborane, and so is the procedure of calculation.[11] The normal vibrations were treated by Wilson's GF matrix method.[12] The methyl group of this molecule was assumed to be a single dynamic unit. This molecule has eight symmetry species. The B_{1u}, B_{2u} and B_{3u} vibrations are infrared-active, and the A_{1g}, B_{1g}, B_{2g} and B_{3g} vibrations are Raman-active, but the A_{1u} vibration is inactive.

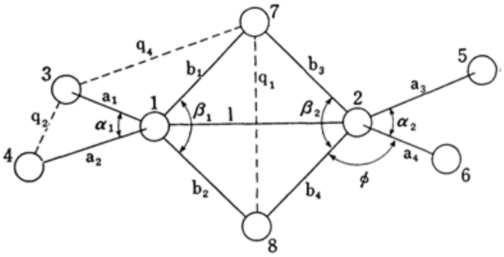

Fig. 1. The structure of the trimethylaluminum molecule, indicating the numbering of the atoms and the internal coordinates.
1, 2, Al; 3, 4, 5, 6, 7, 8, CH_3.
ϕ_1 ∠713, ϕ_2 ∠714, ϕ_3 ∠813, ϕ_4 ∠814,
ϕ_5 ∠826, ϕ_6 ∠825, ϕ_7 ∠726, ϕ_8 ∠725
τ_1 8172, τ_2 8271, τ_3 7182, τ_4 7281

The internal coordinates are also given in Fig. 1. The symmetry coordinates were constructed as linear combinations of the internal coordinates, $\boldsymbol{S}=\boldsymbol{UR}$. The orthogonal $\boldsymbol{U}$ matrices have been described previously.[11] A modified Urey-Bradley potential function was assumed as follows;

$$\begin{aligned}2V=&\sum_{i=1}^{4}K_a(\Delta a_i)^2+\sum_{i=1}^{4}K_b(\Delta b_i)^2+K_l(\Delta l)^2\\&+\sum_{i=1}^{2}H_\alpha(a\Delta\alpha_i)^2+\sum_{i=1}^{2}H_\beta(b\Delta\beta_i)^2\\&+\sum_{i=1}^{8}H_\phi(b\Delta\phi_i)^2+\sum_{i=1}^{4}H_\tau(b\Delta\tau_i)^2\\&+2tb^2(\Delta\phi_1\Delta\phi_7-\Delta\phi_1\Delta\phi_8+\Delta\phi_2\Delta\phi_3\\&-\Delta\phi_2\Delta\phi_7+\Delta\phi_3\Delta\phi_5-\Delta\phi_3\Delta\phi_6+\Delta\phi_4\Delta\phi_6\\&-\Delta\phi_4\Delta\phi_5)+\sum_{i=1}^{11}F(\Delta q_i)^2\end{aligned}\qquad(1)$$

where K, H and F are stretching, bending and repulsive constants respectively, and t is the trans-interaction constant (the cis-interaction constant was set as equal to $-t$). There are three kinds of short $CH_3\cdots CH_3$ distances, as Fig. 1 shows. However, since their intergroup distances are nearly equal, a common repulsion constant, F, was used. The linear repulsion term, $F'(=-F/10)$, was omitted. The interaction terms, k_1, f_1 and f_2, in the potential function of diborane[11] were not included in the

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[11] T. Ogawa and T. Miyazawa, *Spectrochim. Acta*, **20**, 557 (1964).

[12] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

present treatment because available experimental data were not sufficient for determining these terms. Although there were apparently nine parameters in the present potential function, H_β was set as zero (cf. diborane11)) and H_τ was assumed to be 0.02 md./Å. The seven remaining potential parameters were adjusted by the least-squares treatment.13) A NEAC 2101 computer (Nippon Electric Company, Tokyo) was used for the numerical calculation.

Results and Discussion

The vibrational assignments made by Hoffmann,4) Ogawa et al.,6) Gray8) and Onishi et al.9) are shown in Table I, together with the observed spectra and the present assignments.

As was shown in our previous paper,10) no band was found in the region 400—65 cm^{-1} except for the two at 367 and 175 cm^{-1}. All the vibrations except the puckering mode, ν_{10}, are expected to lie in the region above 65 cm^{-1}. The rocking mode, ν_9, may well, however, be very weak, since the corresponding band of diborane has not yet been observed.14) Nevertheless, Hoffmann's assignments need three bands in this region, whereas Gray's assignments need only two. In this respect, Gray's assignments give a one-to-one correspondence between the observed bands and the expected vibrations.

One of the characteristics of Gray's assignments is that the frequencies of the infrared-active vibrations are appreciably higher than those of the corresponding Raman-active vibrations. That makes it very difficult to construct a reasonable potential function and to determine the force constants satisfactorily. A set of Urey-Bradley force constants always predicts higher frequency values for ν_1, ν_2 and ν_3 than those for ν_{16}, ν_{17} and ν_{18} respectively, partly because some of the diagonal $\boldsymbol{G}$ matrix elements for the A_{1g} species are larger than the corresponding elements for the B_{3u} species. Therefore, Gray's assignments of Raman lines were tentatively modified; the weak line at 632 cm^{-1} or 725 cm^{-1} was assigned to ν_1, and the lines at 592 cm^{-1}, 453 cm^{-1} and 313 cm^{-1} were assigned to ν_2, ν_3 and ν_4 respectively. In some preliminary calculations, however, it was not yet possible to obtain a reasonable potential function in accordance with such assignments.

The isotope shifts of vibrational frequencies have been measured by Gray and used in discriminating the skeletal vibrations from methyl vibrations. Thus, the infrared band at 616 cm^{-1} was assigned to ν_{16},8) although in previous studies4-7,9) the band at 562 cm^{-1} had been assigned to ν_{16}. The infrared band at 772 cm^{-1} had been assigned to ν_8 by Gray.8) However, this frequency appears to be too high for a skeletal vibration. Accordingly, the band at 697 cm^{-1} was again assigned to ν_8 in the present study.

Onishi and Shimanouchi9) assigned the infrared band at 367 cm^{-1} to ν_{17}, and the Raman lines at 153 and 185 cm^{-1}, to ν_4 and ν_{12} respectively. They treated the skeletal vibrations on the basis of the Urey-Bradley field modified

TABLE I. THE OBSERVED SPECTRA AND THEIR ASSIGNMENTS

			Hoffmann4)	Ogawa et al.6)	Gray8)	Onishi et al.9)	Present Study
Raman active	A_{1g}	ν_1 (Str.)	592	592	592	592	592
		ν_2 (Str.)	453	453	453	453	453
		ν_3 (Ring.)	313	313	313	313	313
		ν_4 (Bend.)				153	153
	B_{1g}	ν_6 (Str.)			495?		
		ν_7 (Wag.)					
	B_{2g}	ν_{11} (Str.)	683	683	683	683	683
		ν_{12} (Rock.)				185	
	B_{3g}	ν_{15} (Twist.)					185?
Infrared active	B_{1u}	ν_8 (Str.)	696	697	772	696	697
		ν_9 (Rock.)		171?			
		ν_{10} (Puck.)					
	B_{2u}	ν_{13} (Str.)	480	487	652?	479	480
		ν_{14} (Wag.)		200?*			175
	B_{3u}	ν_{16} (Str.)	564	562	616	565	616
		ν_{17} (Str.)		369	480	367	367
		ν_{18} (Bend.)		304*	369		175

?: Questionable assignments.
*: These bands were found in the present study to be due to impurities.

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13) D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano, *J. Chem. Phys.*, **27**, 43 (1957).

14) W. L. Smith, I. M. Mills, ibid., **41**, 1479 (1964).

TABLE II. THE OBSERVED AND CALCULATED FREQUENCIES OF TRIMETHYLALUMINUM AND DEUTERATED TRIMETHYLALUMINUM (cm^{-1})

			$Al_2(CH_3)_6$		$Al_2(CD_3)_6$	
			Obs.[a)]	Calcd.	Obs.[b)]	Calcd.
Raman active	A_{1g}	ν_1	592	633		608
		ν_2	453	473		436
		ν_3	313	305		287
		ν_4	153	145		132
	B_{1g}	ν_6		395		378
		ν_7		210		198
	B_{2g}	ν_{11}	683	690		659
		ν_{12}		173		163
	B_{3g}	ν_{15}	185	186		169
Infrared active	B_{1u}	ν_8	697	688	677	657
		ν_9		257		237
		ν_{10}		48		44
	B_{2u}	ν_{13}	480	478	435	452
		ν_{14}	175	173		163
	B_{3u}	ν_{16}	616	583	579	544
		ν_{17}	367	358	315	334
		ν_{18}	175	183		170
Inactive	A_{1u}	ν_5		151		138
$\|\bar{\delta}\|$	(%)			3.0		
$(\bar{\delta^2})^{1/2}$	(%)			3.7		

a) Raman lines: Ref. 4, infrared bands: Refs. 4, 6 and 10.
b) Ref. 8.

TABLE III. THE DIAGONAL ELEMENTS OF POTENTIAL ENERGY DISTRIBUTION ($F_{ii}L^2_{ia}/\lambda_a$)*

A_{1g}	S_1^a	S_2^b	S_3^l	S_4^α	S_5^ϕ
ν_1	73	14	21	2	0
ν_2	20	67	10	1	1
ν_3	8	24	59	9	0
ν_4	0	2	9	61	32

B_{1g}	S_8^b	S_9^ϕ
ν_6	108	3
ν_7	2	107

B_{2g}	S_{13}^a	S_{14}^ϕ
ν_{11}	103	4
ν_{12}	0	99

B_{1u}	S_{10}^a	S_{11}^ϕ	S_{12}^τ
ν_8	103	2	1
ν_9	0	56	44
ν_{10}	2	47	55

B_{2u}	S_{16}^b	S_{17}^ϕ
ν_{13}	110	8
ν_{14}	0	102

B_{3u}	S_{20}^a	S_{21}^b	S_{22}^α	S_{23}^ϕ
ν_{16}	101	3	1	0
ν_{17}	0	88	2	2
ν_{18}	1	1	73	28

* The superscripts indicate internal coordinates. See Fig. 1.

with the resonance term. This term mainly affects the ν_6 vibration, which has not been observed experimentally for trimethylaluminum. Accordingly, this term was not included in the present potential function.

In the present study the vibrational assignments were carried out with reference to the results of the frequency calculation. As for the Raman bands at 683, 592, 453 and 313 cm^{-1}, Hoffmann's assignments were used. The ν_4 vibration is expected to be very strong, since this vibration belongs to the totally-symmetric species and since the corresponding Raman line of diborane is very strong. In agreement with Onishi's assignment, the strong line at 153 cm^{-1} was thus assigned to ν_4, although it is practically depolarized. As in the case of diborane, the B_{1g} vibrations are not expected to be very strong. Two other Raman-active vibrations, ν_{12} and ν_{15}, are also expected to lie above 70 cm^{-1}. In the case of diborane, the ν_{12} vibration has not been observed in the Raman effect, whereas the ν_{15} Raman vibration was of medium intensity. Accordingly, the Raman line of trimethylaluminum at 185 cm^{-1} was tentatively assigned to the ν_{15} mode.

(This line had been assigned to ν_{12} by Onishi and Shimanouchi.[7,9]) The infrared bands at 697, 480 and 616 cm^{-1} were assigned to ν_8, ν_{13} and ν_{16} respectively, as has been mentioned before. Some of the preliminary assignments[6] were revised in consideration of refined experimental results,[10] and the bands at 367 and 175 cm^{-1} were assigned to ν_{17} and ν_{18} respectively.

The results of the normal vibration calculation are shown in Table II, both for trimethylaluminum and for the fully deuterated derivative. The calculated ν_{14} frequency lies near ν_{18} with the present potential field. Accordingly, the observed frequencies of the ν_{14} and ν_{18} vibrations were both taken to be 175 cm^{-1}. The ν_{12} vibration calculated at 173 cm^{-1} may partly contribute to the broad Raman band at 153—185 cm^{-1}. The potential energy distributions $(F_{ii}L_{ia}^2/\lambda_a)$[15] for trimethylaluminum are shown in Table III.

TABLE IV. THE CALCULATED FORCE CONSTANTS AND THEIR STANDARD ERRORS

	Calculated values md./Å	Standard errors		
		σ_1	σ_2	σ (total)
K_a	2.16	0.04	0.14	0.15
K_b	0.88	0.02	0.03	0.04
K_l	1.24	0.07	0.22	0.23
H_α	0.054	0.003	0.013	0.013
H_β	0	—	—	—
H_ϕ	0.040	0.006	0.016	0.017
H_τ	0.020	—	—	—
t	0.013	0.001	0.000	0.001
F	0.080	0.010	0.030	0.032

σ_1; Standard errors which arise from experimental uncertainties.

σ_2; Standard errors which arise from deficiencies in the physical model of the potential field.

The force constants adjusted by the least-squares refinements are shown in Table IV, together with their standard errors. As was indicated by preliminary calculations of trimethylaluminum and diborane,[6] the frequency fit was improved by a decrease in the value of the bending constant, H_β. Therefore, this constant, H_β, was also set as equal to zero. There are no experimental data on the puckering vibration; accordingly, the value of H_τ was set arbitrarily at 0.02 md./Å. The trans- and cis-interaction terms were introduced rather arbitrarily and set so as to yield the best agreement between the observed and the calculated ν_{15} frequencies. Without these interaction terms, the ν_5 and ν_{12} frequencies would be considerably lower than the calculated values and the ν_9 and ν_{15} frequencies, higher than the calculated values.

The standard errors of potential constants were calculated by the formula:[11]

$$\sigma^2(K_h)=\frac{n}{n-q}\times\{(\boldsymbol{J}^*\boldsymbol{W}\boldsymbol{J})^{-1}\boldsymbol{J}^*\boldsymbol{W}\rho^2\boldsymbol{W}\boldsymbol{J}(\boldsymbol{J}^*\boldsymbol{W}\boldsymbol{J})^{-1}\}_{hh} \quad (2)$$

where n and q are the numbers of the observed frequencies and adjustable force constants respectively. $\boldsymbol{J}$ is the Jacobian matrix, and ρ is the diagonal matrix of the residuals between the calculated and the observed data. In the calculation of standard errors of potential constants, the standard errors of the observed frequencies were assumed to be one per cent.

The similarity of the molecular structure of trimethylaluminum to that of diborane was repeatedly used in the vibrational assignments or normal vibration treatments. The formula of the potential function and also the relation of the magnitude of the potential constants are similar in the two molecules. However, the methyl group of trimethylaluminum is larger than the hydrogen atom of diborane, and the mutual repulsion terms among methyl groups were taken into account.

In the present potential function, there were several characteristics which were similar to those of diborane. The first was that the terminal-bond stretching constant (K_a) was more than twice as great as the bridge-bond stretching constant (K_b). This shows that the bridge half-bond was considerably weaker than the terminal single bond. The second was that in-plane angle-deformation potential terms (H_β) of the bridge may be neglected in the potential function of this molecule. The bridge bond was not expected to have much directional property, and the infinitesimal change in the bridge angle was not expected to be confronted by a strong restoring force. The third was that the stretching constant (K_l) between two aluminum atoms was large enough for us to confirm the existence of a bond between them. In fact, the interatomic distance, 2.57 Å, is approximately equal to the sum (2.52 Å) of Pauling's tetrahedral covalent radii.[2,16]

Because of the lack of enough observed data for deuterated species, the values of the standard errors of the potential constants were greater than those in the case of diborane, but they were nevertheless satisfactory since all constants were essentially determined.

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[15] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1952): I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 243 (1953).

[16] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, U. S. A. (1960), p. 246.

The present assignments were finally set on the basis of Hoffmann's assignments, taking Gray's data on isotope shift into consideration.

Summary

A vacuum infrared cell for reactive or intermediate species has been devised by the use of polyethylene sheets as optical windows. The infrared spectra in the 4000—3100 cm^{-1}, 2500—1500 cm^{-1}, 1250—750 cm^{-1} and 700—65 cm^{-1} regions can be measured with this liquid cell.

The vibrational assignments of the observed spectra have been carried out. The band at 367 cm^{-1} has been assigned to ν_{17}, and the band at 175 cm^{-1}, to ν_{18} and ν_{14}.

The normal vibrations have been calculated, and the potential function of this molecule has been studied. A bond has been concluded to lie between two aluminum atoms. The characteristics of the potential function and the bond structure of trimethylaluminum have also been discussed.

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