

THE MILLIMETER AND SUBMILLIMETER SPECTRUM OF AlCH_3 ($\tilde{X}^1A_1$)

J. S. ROBINSON¹ AND L. M. ZIURYS²

Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604

Received 1996 August 8; accepted 1996 September 18

ABSTRACT

The pure rotational spectrum of AlCH_3 has been recorded using millimeter/submillimeter direct absorption techniques. This is the first time this species has been observed in the laboratory by any spectroscopic method. AlCH_3 was created in a d.c. discharge by the reaction of aluminum vapor and dimethyl mercury. The $K = 0, 1, 2$, and 3 components in fourteen rotational transitions of this symmetric top molecule were measured in the frequency range 188–517 GHz and several lines recorded for $K = 4, 5$ and 6 ladders as well. From these data, rotational parameters have been accurately determined. This study confirms the structure predicted for AlCH_3 from theoretical calculations, as well as provides precise rest frequencies. Aluminum-bearing molecules have been observed in the late-type carbon star IRC +10216, which also has a large abundance of CH_4 . Hence, AlCH_3 may be detectable in this object and perhaps in other sources.

Subject headings: ISM: molecules — line: identification — molecular data — methods: laboratory

1. INTRODUCTION

To date, two molecules containing aluminum have been observed in the interstellar medium, specifically towards the circumstellar envelope of the late-type carbon star IRC +10216 (Cernicharo & Guélin 1987; Ziurys, Apponi, & Phillips 1994). These two species, AlCl and AlF , are rather unexpected because both contain a halogen atom, and the abundances of this element group are not high. For example, the cosmic abundance of chlorine is $\text{Cl}/\text{H}_2 \sim 6 \times 10^{-7}$, and that of fluorine is $\text{F}/\text{H}_2 \sim 1 \times 10^{-7}$. Both AlF and AlCl , however, appear to be present exclusively in the inner part of the circumstellar shell (Cernicharo & Guélin 1987; Ziurys et al. 1994; Guélin et al. 1995), where dredge-up events associated with helium-shell burning maybe enhancing the abundances of the halide elements (e.g., Mathews 1992). Moreover, temperatures and densities are much higher in the inner shell than what is typically found in molecular clouds such that the chemistry in this region is thermodynamically rather than kinetically controlled (e.g., Glassgold 1996). The formation of very stable, highly ionic, closed-shell halide species may be favored in such an environment (e.g., Tsuji 1973).

A molecule bearing aluminum has yet to be found in the outer part of the envelope, where temperatures and densities are more similar to dense clouds (Glassgold 1996). Such a result is curious, since radicals bearing magnesium are relatively abundant in this material, as the detection of MgNC , its magnesium 25 and 26 isotopomers and its metastable form, MgCN , indicate (e.g., Guélin et al. 1995; Ziurys et al. 1995). The distribution of inner envelope species as opposed to those present in the outer part must be an important key to unraveling the chemical processes producing metal-containing compounds, be it ion-molecule reactions, photochemistry, evaporation from grains, or other pathways.

On the other hand, aluminum has a relatively high melting point and can be very corrosive in the gas phase and is therefore difficult to work with in the laboratory. Consequently, only a few simple aluminum compounds have been

studied in the gas phase using high resolution spectroscopy. Among the molecules investigated include AlO (Yamada et al. 1990), AlS (Takano, Yamamoto, & Saito 1991), AlH (e.g., Goto and Saito 1995), and AlOH (Apponi, Barclay, & Ziurys 1993), as well as AlF and AlCl (e.g., Wyse, Gordy, & Pearson 1970). Two of these species are unlikely to be very abundant in a carbon-rich envelope (AlO , AlOH), and the rotational transitions of AlH are inaccessible by ground-based astronomy. This process of elimination leaves only AlS as a viable possibility for detection in IRC +10216 and other carbon-rich stars. Clearly there are other molecules containing aluminum that are possible candidates but whose rest frequencies are unknown.

One Al-containing molecule that is perhaps observable in IRC +10216 and in other circumstellar and interstellar sources is aluminum monomethyl, AlCH_3 . It has already been well-established that CH_4 is a prevalent species in the envelope of IRC +10216 from infrared observations (Hall & Ridgway 1978), with an abundance, relative to CO , of $\sim 2 \times 10^{-3}$. Because of its high stability, methane is likely to be produced in the inner shell of IRC +10216 by LTE chemistry and survive transport to the outer envelope. As postulated for other stable carbon bearing species such as HCN and HCCH , CH_4 is probably photo-dissociated in the outer shell, resulting in radicals and ions like CH_3 , CH_2 , and CH_4^+ (e.g., Glassgold 1996). These photodissociation products lead to CH_3CN (an outer envelope molecule), and could also produce AlCH_3 .

In this paper we present the first laboratory detection of AlCH_3 and measurement of the pure rotational spectrum of its ground electronic state, 1A_1 . Previous to this work, only theoretical calculations existed for this organoaluminum compound, primarily the work of Schaefer and collaborators (Fox et al. 1980; Jin, Xie, & Schaefer 1990, 1991). There was also some evidence for the existence of AlCH_3 from mass spectroscopic detection of AlCH_3^+ (Srinivas, Sülzle, & Schwarz 1990). In this study, fourteen rotational transitions of AlCH_3 , a symmetric top species, were recorded in the range 188–517 GHz, including measurement of several K components in every transition. Rotational constants have been accurately determined for this molecule, which result in structural parameters in excellent agreement with the predictions of Schaefer and co-workers. In

¹ NASA Space Grant Fellow.

² Current address: Departments of Astronomy and Chemistry, and Seward Observatory, University of Arizona, Tucson, AZ 85721.

this work we present our measurements and briefly discuss the structure of AlCH_3 .

2. EXPERIMENTAL

The rotational transitions of aluminum monomethyl were recorded using one of the millimeter/submillimeter spectrometers of the Ziurys group. To summarize, the instrument consists of a Gunn oscillator/Schottky diode multiplier source, a reaction chamber, and an InSb detector. Data collection is controlled by a PC (see Ziurys et al. 1994). Radiation from the source is propagated quasi-optically through the reaction cell (a double-pass system) and into the detector through a series of teflon lenses and a polarizing grid. The Gunn oscillator is modulated at a rate of 25 kHz for phase-sensitive detection; signals are detected at 2f using a lock-in amplifier.

AlCH_3 was synthesized by the reaction of aluminum vapor and $\text{Hg}(\text{CH}_3)_2$, under DC discharge conditions. This technique is the same method that we have employed to create other metal monomethyl compounds (e.g., Anderson & Ziurys 1995). The aluminum vapor was produced in a Broida-type oven and entrained in argon carrier gas, added through the bottom of the oven. Approximately 10 mtorr of dimethyl mercury and 10 mtorr of argon were used, and the discharge required 750 mA at 20–30 volts. The reaction plasma did not exhibit any chemiluminescence probably because the atomic transitions of aluminum are in the ultraviolet region. $\text{Sn}(\text{CH}_3)_4$ and $\text{Si}(\text{CH}_3)_4$ also produced AlCH_3 signals under nearly the same conditions, but they were considerably weaker. Individual transitions of AlCH_3 were recorded using scans 3 MHz wide, obtained by averaging data taken in increasing and decreasing frequency. Linewidths varied from 600 kHz at 188 GHz to 1200 kHz at 517 GHz. Experimental accuracy is estimated to be ± 50 kHz.

3. RESULTS

The frequencies recorded for AlCH_3 in its $^1\text{A}_1$ ground state are presented in Table 1, a total of 65 individual measurements. As mentioned, AlCH_3 is a prolate symmetric top and hence has a C_{3v} symmetry axis. Quantization of rotational angular momentum, indicated by quantum number J , along this axis results in K ladder structure for every transition $J \rightarrow J + 1$, where $K \geq J$. In this study of AlCH_3 , the frequencies of the $K = 0, 1, 2$ and 3 components were measured for all fourteen transitions studied. For the $J = 13 \rightarrow 14$, $J = 19 \rightarrow 20$, and $J = 20 \rightarrow 21$ transitions, the $K = 4, 5$, and 6 lines were additionally observed. These extra components were recorded in order to obtain a better estimate of K -dependent centrifugal distortion parameters. There was possible evidence of aluminum quadrupole splitting in the $K = 3$ component of the $J = 7 \rightarrow 8$ and $J = 8 \rightarrow 9$ transitions.

A typical spectrum obtained for AlCH_3 is shown in Figure 1, which presents the $J = 13 \rightarrow 14$ transitions near 329 GHz. Here the pattern observed for each transition is illustrated. The K components are readily resolved and separated in frequency according to the ratio 1:3:5:7 for $K = 0, 1, 2, 3$, and 4. The progression with increasing K shifts to lower frequency because the centrifugal distortion parameter $D_{JK} > 0$. The $K = 3$ line is approximately a factor of 2 stronger in intensity than the other components due to ortho/para statistics of the methyl hydrogen atoms. (The $K = 6$ component also appeared stronger relative to $K = 5$ and 4).

The data in Table 1 were fit to a ^1A Hamiltonian, which only

TABLE 1
OBSERVED TRANSITION FREQUENCIES OF
 $\text{AlCH}_3: \tilde{X}^1\text{A}_1 (v = 0)$

$J \rightarrow J'$	K	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
$7 \rightarrow 8$	0	188257.801	0.017
	1	188246.423	0.010
	2	188212.323	0.009
	3	188155.131	...
$8 \rightarrow 9$	0	211777.551	0.035
	1	211764.748	0.017
	2	211726.363	-0.029
	3	211662.191	...
$9 \rightarrow 10$	0	235292.818	-0.021
	1	235278.632	-0.010
	2	235236.087	0.014
	3	235165.171	-0.018
$10 \rightarrow 11$	0	258803.257	-0.006
	1	258787.620	-0.038
	2	258740.886	0.020
	3	258662.918	-0.035
$11 \rightarrow 12$	0	282308.297	-0.002
	1	282291.274	-0.015
	2	282240.260	-0.025
	3	282155.363	0.006
$12 \rightarrow 13$	0	305807.469	0.013
	1	305789.077	0.032
	2	305733.808	-0.032
	3	305641.937	0.021
$13 \rightarrow 14$	0	329300.259	0.014
	1	329280.437	<0.001
	2	329221.065	0.023
	3	329122.131	-0.010
	4	328983.889	0.014
	5	328806.454	0.016
$14 \rightarrow 15$	6	328590.063	-0.017
	0	352786.176	<0.001
	1	352764.973	-0.002
	2	352701.390	-0.012
	3	352595.557	0.011
	4	352500.063	<0.001
$15 \rightarrow 16$	0	376264.759	<0.001
	1	376242.168	-0.002
	2	376174.445	0.012
	3	376061.646	0.002
	4	423197.938	0.016
	5	423172.564	-0.007
$17 \rightarrow 18$	6	423096.537	-0.013
	0	422969.970	0.001
	1	446651.495	-0.028
	2	446624.803	0.006
	3	446544.667	0.007
	4	446411.248	0.026
$18 \rightarrow 19$	0	470095.820	0.005
	1	470067.730	0.007
	2	469983.485	0.001
	3	469843.217	-0.002
	4	469647.102	-0.023
	5	469395.471	-0.010
$19 \rightarrow 20$	6	469088.695	0.051
	0	493530.311	<0.001
	1	493500.862	0.005
	2	493412.493	-0.042
	3	493265.458	-0.014
	4	493059.872	-0.003
$20 \rightarrow 21$	5	492796.063	0.026
	6	492474.284	-0.048
	0	516954.527	0.007
	1	516923.713	0.003
	2	516831.331	0.006
	3	516677.511	0.016

models rotational parameters as there are no unpaired electrons involved in AlCH_3 . (The two lines with possible quadrupole structure were not included in the fit.) The resulting

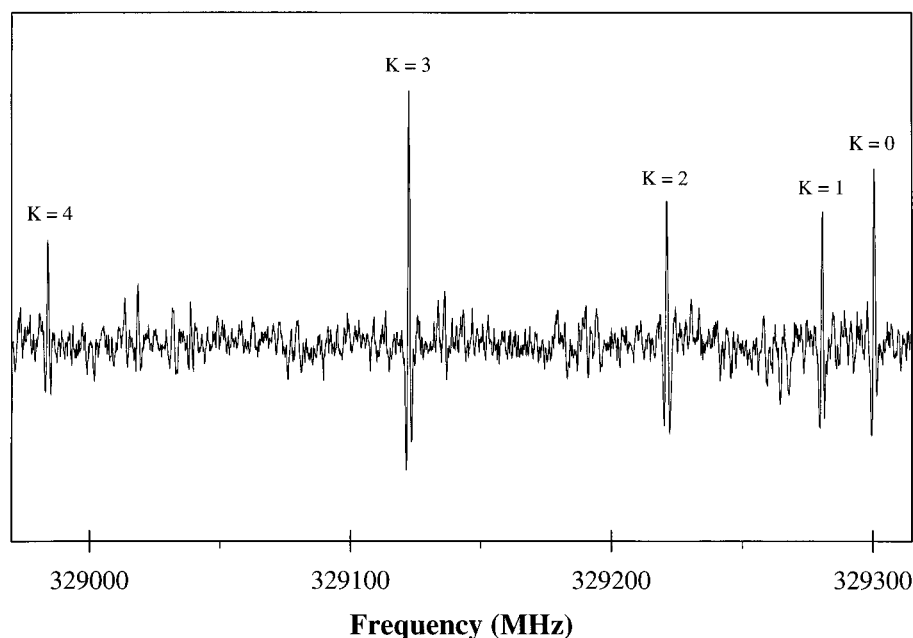


FIG. 1.—Spectrum of the $J = 13 \rightarrow 14$ rotational transition of AlCH_3 observed in this work near 329 GHz. Because this molecule is a symmetric top, each transition is composed of K components, several of which are visible in the data. This spectrum was created from a composite of four scans, each 100 MHz in coverage and 1 minute in duration.

constants are presented in Table 2. As the table shows, in addition to the rotational constant B , first order centrifugal distortion parameters (D_J and D_{JK}) and two second-order corrections (H_{KJ} and H_{JK}) were determined. Because transitions only within K ladders were observed in this work (i.e., $\Delta K = 0$), the rotational constant A , and parameters D_K and H_K could not be established; they require measurement of transitions crossing K ladders. The resulting rotational constant is in good agreement (within 150 MHz) of the theoretical prediction by Jin et al. (1990), also listed in the table.

The errors quoted in Table 2 are 3σ and are based solely on the statistics of the analysis. However, the errors do suggest that all five parameters used in the fit are well determined. Also, these constants reproduce the observed frequencies to residuals of $\nu_{\text{obs}} - \nu_{\text{calc}} \leq 50$ kHz, i.e., within the experimental uncertainty.

4. DISCUSSION

These measurements will now enable astronomical observations to be conducted for AlCH_3 . Although our searches for MgCH_3 in interstellar gas have so far proved negative (Apponi et al. 1997), this result does not imply that AlCH_3 is not

detectable. Methane is quite prevalent in IRC + 10216, and in molecular clouds in general, and formation of AlCH_3 from CH_4 is a likely production route.

Another important result is that this study has confirmed the structure predicted for AlCH_3 in its ground state by Jin et al. (1990, 1991) and Fox et al. (1980). Using a very high level of calculation (self-consistent field [SCF] and configuration interaction, including single and double excitation [CISD]), these authors derived a symmetric top structure for AlCH_3 , which consists of the aluminum atom bonded to a methyl group. They obtained a Al—C—H bond angle of 111.7° and an aluminum-carbon equilibrium bond length of $r_{\text{Al—C}} = 1.994$ Å, using their highest level of theory. (The carbon-hydrogen bond distance in this case was $r_{\text{C—H}} = 1.090$ Å).

AlCH_3 is a symmetric top and hence has two rotational constants, A and B , from which the $r_{\text{Al—C}}$ and $\theta_{\text{Al—C—H}}$ can be determined, if $r_{\text{C—H}}$ is assumed. Unfortunately in this work only B could be established. Hence, to compare with the theoretical predictions, it was assumed that $r_{\text{C—H}} = 1.090$ Å and $\theta_{\text{Al—C—H}} = 111.7^\circ$. The resulting aluminum-carbon r_0 bond length is $r_{\text{Al—C}} = 1.980$ Å. This value agrees well with the theoretical prediction. Moreover, it is very close to the Al—C bond distance of $1.957(3)$ Å found for $\text{Al}(\text{CH}_3)_3$ from electron-diffraction studies (Alemning, Halvorsen, & Haaland 1971). As pointed out by Fox et al. (1980), the Al atom is trivalent in $\text{Al}(\text{CH}_3)_3$ and hence only single bonds between aluminum and carbon can exist in this molecule. The close agreement between the trimethyl aluminum distance (1.96 Å), and the experimental (1.98 Å) and theory (1.99 Å) values for AlCH_3 indicates that a single bond also exists between the aluminum and carbon for aluminum monomethyl. A double bonded scheme would involve a much shorter distance of ~ 1.7 Å (Jin et al. 1991).

Another possible structure for this compound is $\text{HAl} = \text{CH}_2$, which involves a double bond to carbon. Jin et al.

TABLE 2
MOLECULAR CONSTANTS FOR AlCH_3 : $\tilde{X}^1A_1$ ($v = 0$)

Constant	Millimeter-wave (MHz) ^a	Theory (MHz) ^b
B_v	11,768.72410 (57)	$\sim 11,615$
D_{JK}	0.712410 (76)	...
D_J	0.02041092 (82)	...
$10^4 H_{KJ}$	0.827 (16)	...
$10^4 H_{JK}$	0.12510 (83)	...

^a Errors reported are 3σ and apply to the last digits quoted.

^b Calculated from equilibrium parameters of Jin et al. 1991.

predict this isomer to be ~ 45 kcal mol⁻¹ higher in energy relative to the Al—CH₃ structure. They also suggest that the monomethyl form might isomerize to HAl = CH₂. In our study of AlCH₃, done in the energetic environment of a d.c. discharge, we saw no evidence of the double-bonded structure, which would have an asymmetric top pattern. Hence, our results prove that AlCH₃ is the most stable isomer and that HAl = CH₂ must lie sufficiently high in energy such that

conversion to this product is not favorable. Finally, it is additional evidence that single bonds between aluminum and carbon are preferred.

This research was supported by NASA grant NAGW 2989 and NSF grant AST-95-03274. J. S. R. thanks the NASA Space Grant Program for his fellowship, and A. J. Apponi for earlier efforts on this project.

REFERENCES

- Alemenningen, A., Halvorsen, S., & Haaland, A. 1971, *Acta Chem. Scand.*, 25, 1937
Anderson, M. A., & Ziurys, L. M. 1995, *ApJ*, 452, L157
Apponi, A. J., Barclay, W. L., Jr., & Ziurys, L. M. 1993, *ApJ*, 414, L129
Apponi, A. J., et al. 1997, in preparation
Cernicharo, J., & Guélin, M. 1987, *A&A*, 183, L10
Fox, D. J., Ray, D., Rubesin, P. C., & Schaefer, H. F., III. 1980, *J. Chem. Phys.*, 73, 3246
Glassgold, A. E. 1996, *ARA&A*, in press
Goto, M., & Saito, S. 1995, *ApJ*, 452, L147
Guélin, M., Forestini, M., Valiron, P., Ziurys, L. M., Anderson, M. A., Cernicharo, J., & Kahane, C., 1995, *A&A*, 297, 183
Hall, D. N. B., & Ridgway, S. T. 1978, *Nature*, 273, 281
Jin, S. Q., Xie, Y., & Schaefer, H. F., III. 1991, *J. Chem. Phys.*, 95, 1834
———. 1990, *Chem. Phys. Lett.*, 170, 301
Mathews, G. J. 1992, *Nature*, 359, 18
Srinivas, R., Sülzle, D., & Schwarz, H. 1990, *J. Am. Chem. Soc.*, 112, 8334
Takano, S., Yamamoto, S., & Saito, S. 1991, *J. Chem. Phys.*, 94, 3355
Tsuji, T. 1973, *A&A*, 23, 411
Wyse, F. C., Gordy, W., & Pearson, E. F. 1970, *J. Chem. Phys.*, 52, 3887
Yamada, C., Cohen, E. A., Fujitake, M., & Hirota, E. 1990, *J. Chem. Phys.*, 92, 2146
Ziurys, L. M., Apponi, A. J., Guélin, M., & Cernicharo, J. 1995, *ApJ*, 445, L47
Ziurys, L. M., Apponi, A. J., & Phillips, T. G. 1994, *ApJ*, 433, 729
Ziurys, L. M., Barclay, W. L., Jr., Anderson, M. A., Fletcher, D. A., & Lamb, J. W. 1994, *Rev. Sci. Instrum.*, 65, 1517