Detection of Ar–CH_4 Complexes in the 7 µm Region by Diode Laser Spectroscopy

I. Pak [1], M. Hepp, D. A. Roth, G. Winnewisser, and K. M. T. Yamada [a]

I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Köln
[a] National Institute for Advanced Interdisciplinary Research (NAIR), Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan

Z. Naturforsch. **51a,** 997–1001 (1996); received May 22, 1996

The absorption spectrum of the Ar–CH_4 van der Waals complex was measured for the first time in the 7 µm region. The complexes were produced in a pulsed slit supersonic jet and detected by a tunable diode laser spectrometer with 40 MHz spectral resolution. The strongest absorption features of the Ar–CH_4 complex were observed in the spectral region 1310.57–1311.05 cm^{-1}, located between the Q(1) and the R(0) lines of the ν_4 fundamental band of the methane monomer. It was found that the newly detected absorption lines belong to three Q-branches of the Ar–CH_4 complex. The transitions of these Q-branches are related to the Q(1) transition in the ν_4 fundamental band of the methane molecule, which can rotate almost freely inside the complex. The three Q-branches have been assigned.

1. Introduction

The spectroscopical investigations of the van der Waals complexes formed by a rare gas atom and a molecule allow one to determine the geometric structure of the complex, the character of the internal motion of the molecule relative to the atom inside the complex, and the intermolecular potential surface with the help of theoretical modeling. The first publications dealing with high resolution spectroscopy in the specific case of a noble gas atom-spherical top molecule have appeared only recently [1–4]. The absorption spectra of Ar–SiH_4 complexes were measured in a supersonic jet by a tunable diode laser (TDL) spectrometer in the 5 µm region and the detailed analysis of these spectra was given by Randall et al. [1, 2]. A similar experimental technique was applied by Urban et al. [3] to the investigation of Ar–SiF_4 and Kr–SiF_4 complexes in the 10 µm region. The recorded spectra showed a very similar structure for both Ar–SiF_4 and Kr–SiF_4 and the analysis of these spectra was given in [3].

In the case of complexes consisting of a noble gas atom and a methane molecule the existing spectroscopical information was not sufficient for a comparison with the results of theoretical calculations [5, 6]. The absorption spectra of Ar–CH_4 and Kr–CH_4 were recorded in the 3 µm region by McKellar using a low temperature long path static cell and a high resolution Fourier transform spectrometer [4]. Although the rotational structure was partly resolved, it was not possible to secure an assignment of the spectrum. The spectrum analysis was additionally complicated by the interference of the complex's lines with strong and broad CH_4 monomer absorption lines in the cell and by the limited spectral resolution (≈ 0.01 cm^{-1}) of the measurements.

In the present study, a TDL-pulsed slit supersonic jet spectrometer was applied for the detection of the Ar–CH_4 spectra in the 7 µm region. The detected transitions of the complexes involved the vibrational transition from the ground to the first excited vibrational state in the ν_4 fundamental mode of the CH_4 monomer.

2. Experimental

A detailed description of the Cologne-supersonic jet spectrometer, which was recently modified for the investigation of the molecular van der Waals complexes, is given elsewhere [7, 8]. Therefore the experimental arrangement and the characteristics of the spectrometer are described only briefly below.

The Ar–CH_4 complexes were produced in the supersonic expansion of a mixture of methane with ar-

---

[1] On leave of absence from the Institute of Spectroscopy, Troitzk, Moscow region, Russia.

Reprint requests to Prof. G. Winnewisser.

0932-0784 / 96 / 0900-0997 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

gon at a stagnation pressure of 2–5 atm through a 15 μm wide slit into a vacuum chamber. Different nozzle units with slit lengths ranging from 7 mm to 40 mm were used. The supersonic jet was pulsed by a modified car fuel injector valve (Bosch) operating at a 80 Hz repetition rate and producing gas pulses with a duration of 2 ms. The expanded gas was evacuated from the chamber by a 250 m^3/h roots pump, which kept the background pressure at a level of 0.1 mbar. A White type multireflection optics was installed inside the vacuum chamber allowing 16 passes of the diode laser radiation through the jet area at a distance of a few mm from the slit nozzle. The wavelength of the TDL was modulated at 10 kHz frequency. After passing through the jet the laser radiation was detected by a HgCdTe detector. The output of the detector-preamplifier system was processed by a lock-in amplifier triggered at the 10 kHz modulation frequency and operated in the $2f$ mode with a time constant of the order of 0.7 ms. The difference between the signals registered with and without absorption in the jet was measured by a boxcar integrator, operated at the 80 Hz frequency of the pulsed jet. The two gates of the boxcar were set to 2.0 ms duration. The time constant of the boxcar was generally chosen in the range 0.1–1.0 s, depending on the frequency scanning rate of the tunable diode laser. This double modulation technique [7] allowed us to reduce significantly both the low frequency excess laser noise and the distortions of the registered base line arising due to unwanted interference effects in the optical scheme of the diode laser spectrometer. An IBM compatible PC together with an AD converter board served to collect the data and to record the spectra.

The spectral resolution in the recorded $Ar-CH_4$ spectra was estimated at 40 MHz, determined by several factors such as residual Doppler broadening of the absorption lines in the slit expansion, frequency jitter of the TDL, additional broadening due to the wavelength modulation of the TDL and the influence of the multireflection optics. The frequency positions of the $Ar-CH_4$ lines were obtained by the simultaneous recording of the N_2O reference spectrum and the fringes of a confocal Fabry-Perot etalon with a free spectral range of 300 MHz. The estimated accuracy of the absolute frequency measurements was 1×10^{-3} cm^{-1}, while the relative positions of the absorption lines recorded within one mode of the diode laser were reproducible within 2×10^{-4} cm^{-1}.

3. Results

The strongest and most conspicuous absorption features of $Ar-CH_4$ are shown in Figure 1. Most of the lines could be attributed to the three Q-branches, which occupy the central spectral range between 1310.57 cm^{-1} and 1311.05 cm^{-1}. The appearance of the three Q-branches is dominated by their obvious different degrees of compactness. The most compact of these Q-branches near 1311.00 cm^{-1} is a fairly common looking Q-branch (Q_0-branch in Table 1) with its head appearing at the low frequency side. The other two Q-branches (Q_-- and Q_+-branches in Table 1) exhibit spacings between lines of the order of 0.01–0.03 cm^{-1}, one order of magnitude smaller than the distance between neighbouring lines which could be expected for the appropriate P- or R-branches of the $Ar-CH_4$ complex. The rotational constant B of the complex can be roughly estimated at 0.1 cm^{-1}, assuming an equilibrium Ar–C separation equal to 3.8–3.9 Å, a value obtained previously from scattering experiments and *ab initio* calculations [5, 9]. Accordingly, in our original assignment it was concluded that these Q_-- and Q_+-branches are indeed Q-branches despite their unusual appearance.

The positions of origin for these two Q-branches were determined by varying the mixing ratio between argon and methane in the jet. We assumed that the rotational temperature of the complexes in the jet should be lower for lower concentrations of methane in argon. At the lower temperature the maximum in the intensity distribution of the absorption lines is shifted towards lower J values. Figure 2 represents the spectra of $Ar-CH_4$ measured with 10% and 0.5% of methane in Ar, respectively. It was found that both Q_-- and Q_+-branches have their origins near 1310.70 cm^{-1}. Measured line positions together with J-assignments for the three Q-branches are listed in Table 1. It should be noted that the first two lines of the Q_0-branch separated by 12 MHz were only partly resolved in the spectrum measured with the jet modulation, i.e. without using the TDL wavelength modulation. From the intensity distributions in the observed Q-branches the rotational temperature was estimated at 5–10 K, depending on ratio of methane and argon in the mixture.

However, change of the Ar/CH_4 mixing ratio bears out another effect concerning the production of different complexes, such as $Ar-CH_4$ and pure methane clusters $(CH_4)_2$. By comparing the upper and the

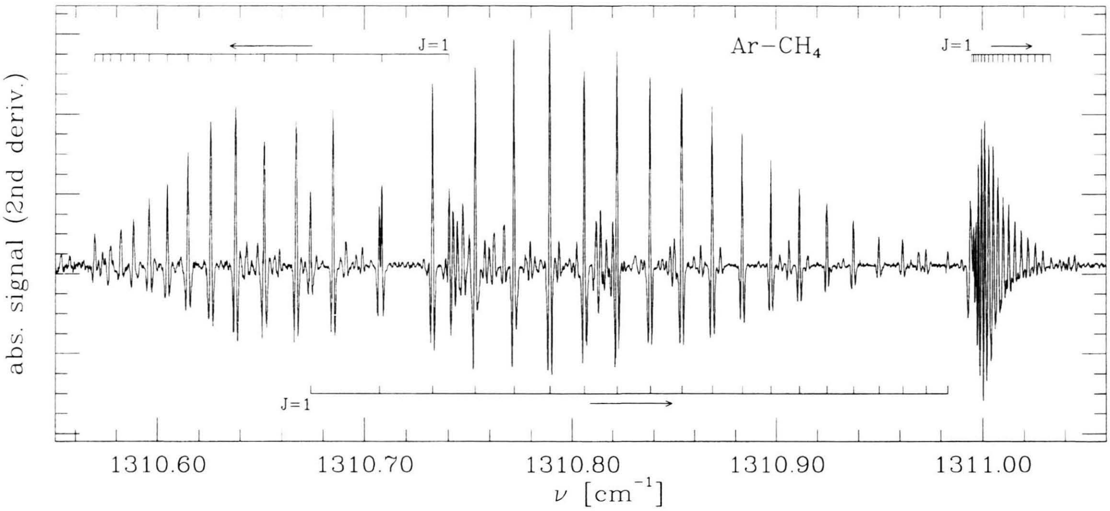

Fig. 1. Detected absorption spectrum of Ar–CH_4 complexes. The depicted wavelength region displays the strongest lines which are attributed to three Q-branches with different compactness. One of these, near 1311.00 cm^{-1} is a "normal" Q-branch (listed as the Q_0-branch in Table 1) with the head at the low frequency side. The other two subbands are also Q-branches (listed as the Q_-- and the Q_+-branches in Table 1) despite their unusual appearance. The *J* assignment is indicated.

lower spectra in Fig. 2 we concluded that some of the weaker lines, for example the lines near 1310.75 cm^{-1} in the upper spectrum, do not belong to Ar–CH_4. They can be attributed to other complexes like $(CH_4)_2$ or higher order cluster of methane. The nature of the observed lines was generally checked by using neon and helium instead of argon in the expansion. Some absorption lines were observed not only with Ar but also with Ne and He and were thus attributed to the higher clusters of methane. It is interesting to note that no lines were measured which could be attributed to Ne–CH_4 or He–CH_4.

4. Discussion

For the investigated complexes containing a rare gas atom and a tetrahedral molecule the same symmetry C_{3v} of the equilibrium geometric structure could be expected [1–4]. Nevertheless, the observed spectra had quite different structures in the three previously examined cases of Ar–SiH_4 [1,2], Ar(or Kr)–SiF_4 [3] and Ar(or Kr)–CH_4 [4], even though the same vibrational mode ν_3 of the tetrahedral molecule was involved in the complex transitions. The spectra of both Ar(or Kr)–SiF_4 and Ar–SiH_4 had regular stucture in the sense that they consisted of separate parallel and perpendicular subbands which were generally composed of a narrow Q-branch with accompanying regularly spaced P- and R-branches. In contrast, such regular structure was not observed in the Ar–CH_4 spectra. Besides the equilibrium geometry of the complex, the spectra are strongly dependant on the character of the internal motion of the tetrahedral molecule inside the complex, which is determined by the anisotropic part of the interaction potential. The observed spectra reveal how strongly the orientation of the spherical top molecule is fixed inside the complex relative to the rare gas atom. In the Ar(or Kr)–SiF_4 case, the potential anisotropy is large enough to prevent the internal rotation of the SiF_4 molecule in the complex. As a result, the spectrum was explained assuming C_{3v} symmetry of the complex [3]. It was shown that in the Ar–SiH_4 case, the silane molecule undergoes hindered rotation [1, 2]. The striking difference between the spectra of the Ar–CH_4 in comparison with Ar–SiH_4 and Ar(or Kr)–SiF_4 allows one to suppose that the methane molecule can rotate even more freely relative to the argon atom in the Ar–CH_4.

The infrared active ν_3 stretching and ν_4 bending vibrations of methane, which have their fundamental bands in the 3 μm and 7 μm regions, respectively, have the same F_2 symmetry of the T_d point group. It is therefore not surprising, that the structure of the Ar–CH_4 spectra observed in the present work in the 7 μm region is of similar appearance to the one ob-

Table 1. The observed Q-branches of Ar–CH_4 (cm^{-1}).

J	Q_--branch	Q_+-branch	Q_0-branch
1	1310.7404	1310.6739	1310.9946
2	1310.7071	1310.7084	1310.9950
3	1310.6849	1310.7326	1310.9958
4	1310.6671	1310.7531	1310.9969
5	1310.6516	1310.7717	1310.9982
6	1310.6377	1310.7892	1310.9996
7	1310.6257	1310.8061	1311.0011
8	1310.6147	1310.8221	1311.0031
9	1310.6048	1310.8382	1311.0051
10	1310.5961	1310.8537	1311.0074
11	1310.5886	1310.8687	1311.0099
12	1310.5822	1310.8833	1311.0127
13	1310.5772	1310.8974	1311.0156
14	1310.5733	1310.9114	1311.0187
15	1310.5695	1310.9247	1311.0220
16		1310.9375	1311.0255
17		1310.9499	1311.0293
18		1310.9615	1311.0331
19		1310.9728	
20		1310.9834	

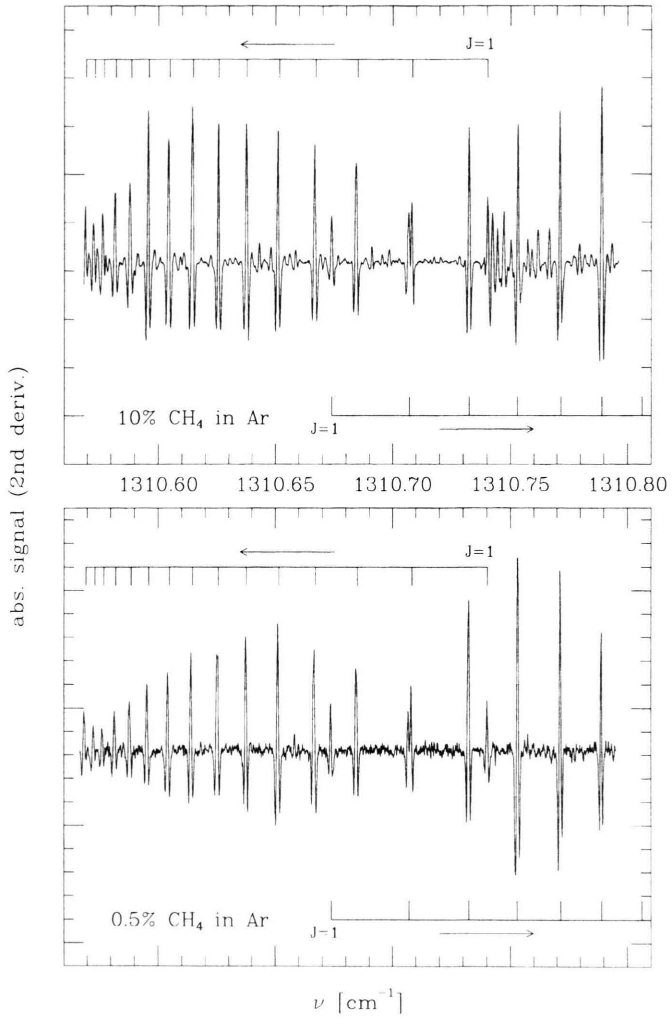

Fig. 2. The influence of the methane concentration on the jet spectrum, registered at a stagnation pressure of 2 atm. The upper and the lower spectra in Figure 2 were recorded with 10% and 0.5% of methane in argon, respectively. It is supposed that the reduction of the amount of methane decreases the rotational temperature of the Ar–CH_4 complexes in the jet. The lower spectrum, which corresponds to a relatively low concentration of methane in argon, shows especially clearly the origin of the Q_+-branch and the whole Q_--branch.

tained in the 3 μm region by McKellar [4]. In both cases the strongest absorption lines were measured in the range between the origin of the Q-branch and the R(0) line of the appropriate fundamentals of free methane. The main absorption features of the spectrum registered by McKellar also seemed to form three partly resolved Q-branches. We note that it was not possible to investigate continuously the whole spectral range close to the center of the ν_4 vibrational band of methane with the diode lasers available to us at present. Consequently, we can not exclude the possibility that other strong absorption lines of the complex could exist in the range. However, no other strong absorption bands of the complex were observed in the FT-spectrum of McKellar in the 3 μm region besides the three Q-branches.

The observed transitions in the present work were assigned as those corresponding to the Q(1) transition in the ν_4 fundamental band of the methane monomer. The appearance of one "normal" Q_0-branch and two "anomalous" Q_-- and Q_+-branches is a consequence of the splitting of the rotational levels of the upper and the lower vibrational state in three components due to the Coriolis interaction between the rotational angular momentum of methane molecule and the end-over-end rotation of the complex. The assignment of the three Q-branches of Ar–CH_4 has recently been substantiated by the detection of a similar Q-branch structure for Kr–CH_4. The positions of the lines listed in Table 1 are well reproduced by a formula similar to the one used for a $^3\Sigma$ state of a diatomic molecule (see, for example, formula 7-6 in [10]). The theoretical explanation for this assignment and the results of the appropriate fit will be given in the next paper.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) for support of this work via Special Research Grant SFB-301. The work of I. P. at Cologne was made possible by the DFG through a grant aimed to support Eastern and Central European Countries and the Republics of the former Soviet Union.

[1] R. W. Randall, J. B. Ibbotson, and B. J. Howard, J. Chem. Phys. **100,** 7042 (1994).
[2] R. W. Randall, J. B. Ibbotson, and B. J. Howard, J. Chem. Phys. **100,** 7051 (1994).
[3] R.-D. Urban, L. G. Jörissen, Y. Matsumoto, and M. Takami, J. Chem. Phys. **103,** 3960 (1995).
[4] A. R. W. McKellar, Faraday Discuss. Chem. Soc. **97,** 69 (1994).
[5] M. M. Szczesniak, G. Chalasinski, and S. M. Cybulski, J. Chem. Phys. **96,** 463 (1992).
[6] J. M. Hutson and A. E. Thornley, J. Chem. Phys. **100,** 2505 (1994).
[7] I. Pak, M. Hepp, R. Phillip, R. Schieder, and G. Winnewisser, Z. Naturforsch. **49a,** 913 (1994).
[8] I. Pak, M. Hepp, D. A. Roth, and G. Winnewisser, Rev. Sci. Instrum. (to be published).
[9] U. Buck, J. Schleusener, D. J. Malik, and D. Secrest, J. Chem. Phys. **74,** 1707 (1981).
[10] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, Dover Publications, New York 1975.