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Vibrational and rotational excitation in a capacitively coupled 13.56 MHz radio frequency CF₄ plasma studied by infrared absorption spectroscopy

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Infrared absorption spectroscopy has been used to determine the vibrational and rotational excitation of CF₄ in a parallel plate plasma etcher. The vibrational and rotational temperatures T_{vib} and T_{rot} of the CF₄ molecules were extracted from the band structure of the ν_3 peak of CF₄ around 1283 cm⁻¹, using a double beam Fourier transform spectrometer. Measurements were performed with and without plasma, at 0.12 cm⁻¹ apodized resolution. From the change of the relative (hot) Q -branch intensities the vibrational temperature was estimated. Furthermore the rotational temperature, which is in these conditions likely to be very close to the gas temperature, was estimated from the shape and intensity of the R branch of the ν_3 peak. It was established that both T_{vib} and T_{rot} have values around 400 and 350 K, respectively. It is therefore concluded that under the studied circumstances the influence of the plasma on T_{vib} is small.

I. INTRODUCTION

In chemically active plasmas several types of particles, such as free radicals and negative and positive ions are produced by dissociation and ionization induced by impact of fast electrons in the plasma. Therefore much of the physics and chemistry of the plasma is determined by the electron energy distribution function (EEDF), and numerous authors study the EEDF theoretically.^{1,2} A factor which can strongly affect the EEDF is the amount of vibrationally excited molecules, since the electrons can gain energy through superelastic collisions.³ Moreover the production of negative ions by resonance dissociative attachment usually can be affected by a high population of vibrationally excited molecules as has been demonstrated^{4,5} for the case of HCl. The rotational excitation is in most cases closely coupled with the gas temperature, which determines in many cases the rate coefficients for chemical reactions between unexcited heavy particles.⁶

Experimental data on the vibrational and rotational excitation mostly come from emission spectroscopy of electronic transitions. For instance, the vibrational and rotational excitation of N₂ impurities in an inductively coupled CF₄ plasma has been measured by van Veldhuizen *et al.*⁷ who found a value of 3000 K for T_{vib} and 550 K for T_{rot} . It is, however, more important to know the vibrational excitation of CF₄ itself, since that is the dominant species in the plasma. This is not possible using emission spectroscopy since CF₄ does not show a line spectrum from which this can be deduced. On the other hand, CF₄ has infrared absorption bands of vibrational transitions which can also be used to measure T_{vib} and T_{rot} . A method to do this is explained in Sec. II.

II. METHOD

In the infrared region between 400–1300 cm⁻¹, CF₄ shows its four fundamental absorption frequencies which are given in Table I. We can see that the ν_2 transition requires the least energy for excitation, i.e., 435 cm⁻¹ (or 53.8 meV). This value is not far from the average energy of the molecules (which is about 26 meV at 300 K). Therefore

even at room temperature some of the lower levels of the ν_2 transition will be significantly populated. This has an effect on the band shape of the ν_3 peak. Besides the normal transition of ν_3 which starts from the ground state, transitions are also possible from vibrationally excited states, such as ν_2 , $2\nu_2$, $3\nu_2$, etc. (see Fig. 1). The Q branches⁸ (with $\Delta J = 0$) of the transitions from these states will in the rest of this paper be denominated as Q_1 , Q_2 , Q_3 , Transitions from excited states are usually known as 'hot bands'.^{8,9} If the potential curve of CF₄ is harmonic the energy difference between the upper level $\nu_3 + n\nu_2$ and the lower level $n\nu_2$ is constant. In this case all hot bands coincide. In practice, however, the potential curve of the CF₄ molecule is slightly anharmonic, which means that the frequency corresponding to these transitions is shifted down a small amount. This results in a ν_3 band shape as depicted in Fig. 2(a) for a measurement without plasma. This band shape is identical to the one obtained by Jones *et al.*⁹ Besides the "normal" ν_3 band located around 1283 cm⁻¹, additional bands occur around 1281 and 1279 cm⁻¹. Since the Q branch is the sharpest feature in the spectrum, the effect of hot bands is most predominant in the occurrence of extra Q bands. The relative intensity of the Q bands is a direct measure for the population of the ν_2 levels relative to the ground state level. If we assume a Boltzmann distribution for the ν_2 levels, the intensity ratio of $\nu_3 + \nu_2 - \nu_2$ over ν_3 [or $I(Q_1)/I(Q_0)$] is equal to a Boltzmann factor $\exp(-h\nu_2/kT_{\text{vib}})$. Moreover, as a result of coupling of the two vibrations, the intensity of the

TABLE I. Fundamental vibrational transitions of CF₄. The values for the frequencies are taken from Ref. 5.

Mode	Frequency (cm ⁻¹)	Degeneracy
ν_1	908.5	1
ν_2	435.0	2
ν_3	1283.2	3
ν_4	631.2	3

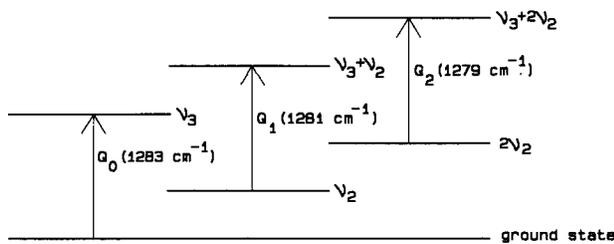


FIG. 1. Schematic representation of the vibrational transitions of CF₄ which are of importance in the context of this study. The intensities of the hot-band transitions are a measure of the population of the ν_2 levels from which they start.

hot band transitions can also be slightly different from the intensity of the ground state transition.⁸ Furthermore the resolution of the measurement is not high enough to resolve the individual rotations in the Q bands, which may cause some errors in the determination of the band intensity. If this is taken into account the intensity ratio for the Q bands can be written as

$$I(Q_0)/I(Q_n) = C_n g_0/g_n \exp(-nhc\nu_2/kT_{\text{vib}}),$$

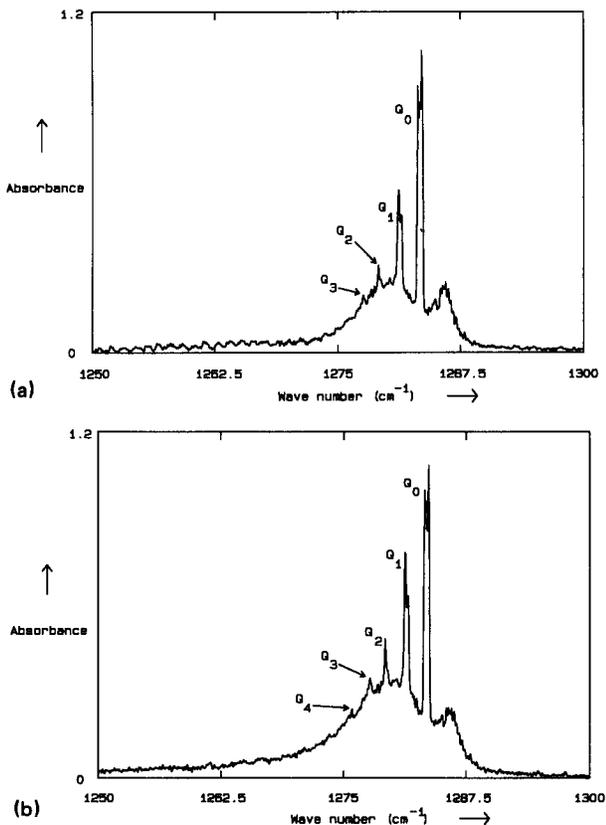


FIG. 2. High-resolution absorption spectrum of the CF₄ ν_3 peak around 1283 cm⁻¹ at 0.12 cm⁻¹ apodized resolution. (a) Without plasma, $T = 300$ K, $p = 50$ mTorr. At 1281 and 1279 cm⁻¹ the hot Q -branch transitions can be seen. The intensity ratio between Q_0 and Q_1 is about 3.27. (b) with plasma, $p = 100$ mTorr. It can be clearly seen that the intensity of the hot Q branches has increased relative to the ground state Q branch. The intensity ratio between Q_0 and Q_1 is now 2.35. From this it follows that the vibrational temperature is higher in the plasma.

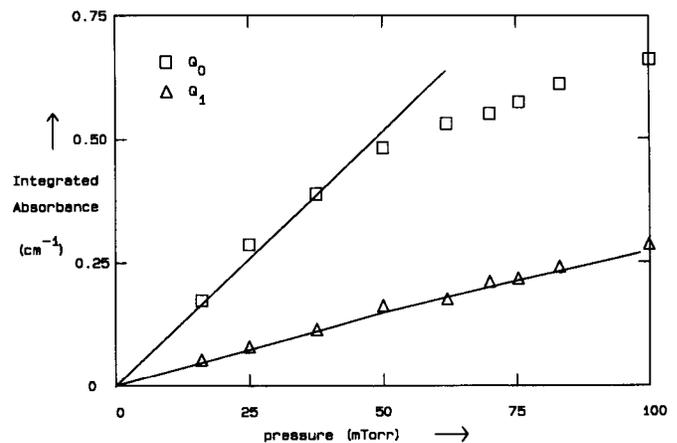


FIG. 3. Calibration curve for relative intensities of the ground state Q branch (Q_0) and the first hot Q branch (Q_1). It follows that the Q_0 intensities are more or less linear with pressure up to $I(Q_0) = 0.5$, whereas $I(Q_1)$ is linear in the whole region investigated.

where Q_n is the Q branch of ν_3 starting from the n th level of ν_2 (see Fig. 1), g_n is the statistical weight of the n th level, h Planck's constant, c the speed of light, k Boltzmann's constant, and C_n a correction factor that accounts for the coupling of the two vibrations, and the effect of the limited resolution. Since the ν_2 transition is doubly degenerated, the statistical weights g_n follow the series⁸

$$g_n = (1, 2, 3, \dots).$$

For $T_{\text{vib}} = 300$ K and C_1 taken to be unity, this yields a value of 4.01 for $I(Q_0)/I(Q_1)$. The measurement was calibrated by measuring $I(Q_0)/I(Q_1)$ as a function of pressure (see Fig. 3). This resulted in a value of 3.27 for a measurement in CF₄ gas at 300 K. The value for the correction factor C_1 is therefore equal to 1.22. The intensity is indeed only slightly influenced by the coupling of the vibrations. If we assume that this factor does not change when the plasma is created, we can calculate T_{vib} in the situation with plasma on from

$$T_{\text{vib}} = \left\{ \ln \left[\frac{I(Q_0)/I(Q_1)|_{\text{plasma on}}}{I(Q_0)/I(Q_1)|_{\text{plasma off}}} \right] \frac{k}{h\nu_2} + \frac{1}{300} \right\}^{-1}.$$

To determine the rotational temperature in the plasma, a simulation of the shape of the R branch of the ν_3 band (corresponding to a transition with $\Delta J = -1$) was fitted on the shape of the experimental R branch (see Fig. 2). The position of the rotational lines of the R branch of transitions from the ground state is given by⁸

$$\nu(J) = \nu_0 + (1 - \zeta_3) 2B_3$$

where ν_0 is the band center frequency, ζ_3 the Coriolis coupling factor for the ν_3 transition and B_3 the rotational constant given by

$$B_3 = \frac{h}{8\pi^2 c I_b},$$

where h is Planck's constant, c the speed of light, and I_b the moment of inertia of CF₄. The Coriolis coupling factor ζ_3 was taken from a measurement of the ν_3 band at 0.03 cm⁻¹ unapodized resolution and was found to be 0.81 in good agreement with literature values.⁹ The intensities of the ro-

tational lines in the R branch can be calculated from⁸

$$I(J) = (2J + 1)^2 \exp[-B_3 J(J + 1)hc/kT_{\text{rot}}].$$

In the simulation also the hot bands were taken into account to fit the experimental data. The rotational temperature could be estimated by taking the best fit to the experimental R branch.

III. EXPERIMENTAL

The infrared absorption spectra have been measured using a double beam Fourier Transform Spectrometer based on a Michelson interferometer. A schematic drawing of the experimental setup is depicted in Fig. 4. The light source of the system is a wall-stabilized arc¹⁰ in Ar which in this spectral region acts as an almost ideal Planck radiator at 13 000 K. The arc light is modulated by a double beam interferometer and after that passes through a vacuum vessel in which two parallel-plate electrodes (12.4 cm diam with an electrode separation of 2.0 cm) driven at 13.56 MHz can be used to produce a plasma. The radio frequency (rf) power is capacitively coupled into the plasma using a matching network and is measured between the generator and the matching network. One of the electrodes and the walls of the vacuum system are held at the ground potential, whereas the other electrode is rf driven. A CF₄ gas flow of 20 sccm was used, resulting in a residence time in the plasma region of about 100 ms. In this way a plasma at 100 mTorr and 100 W rf power was produced, with a sheath thickness of about 8 mm at the rf electrode and about 5 mm at the grounded electrode. Between the beamsplitter and the moving mirror a mirror system has been mounted which makes both optical path lengths equal when the moving mirror is about in the middle of the air bearing over which it moves. This also gives a passive tilt compensation for the tilt of the moving mirror

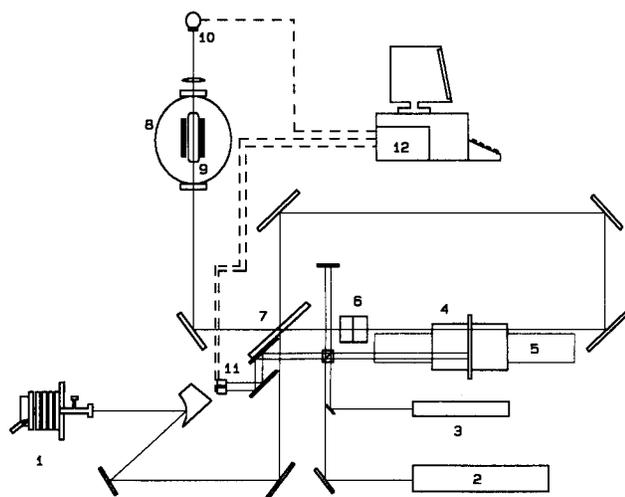


FIG. 4. Experimental setup used in the measurements. It consists of a Fourier transform spectrometer and a parallel-plate plasma etcher. (1) Wall stabilized Ar arc (light source), (2) HeNe laser, (3) white light lamp, (4) moving mirror (driven by a stepper motor), (5) air bearing, (6) periscope system (to enlarge the optical path length), (7) beamsplitter, (8) vacuum vessel, (9) 13.56 MHz rf plasma, (10) MCT detector, (11) detectors for the laser and white light interferometers, (12) PC/AT with a 16-bit ad convertor board.

(similar to the one used by Jennings¹¹). The diameter of the light beam is 5 mm to ensure that the light only passes through the center glow of the discharge. The total absorption length in the system is 25 cm, whereas the plasma diameter (approximately equal to the electrode diameter) is 12.4 cm. Start and trigger pulses for the interferometer are generated by a white light and a (HeNe) laser interferometers that both move parallel to the moving mirror. The interferometer is used in the rapid-scan mode by pulling the moving mirror over an air bearing by a stepper motor. The interferogram is sampled single sided using an Analog Devices RTI-850 ad-converter board mounted in an IBM PC/AT, after which a phase correction routine¹² is used to correct for zero-path errors and dispersion in the system. From the corrected interferogram the spectrum is calculated. It was decided to use an apodized resolution of 0.12 cm⁻¹ to smooth the P and R branches in order to make it easier to estimate the baseline for the Q branches. For the determination of the Q -branch intensities the baseline was formed by the "overall" shape of the R branch. Furthermore, several interferograms (typically 30) were block averaged to improve the signal-to-noise ratio. A cylindrical symmetrical rf plasma was produced by two parallel electrodes at a rf frequency of 13.56 MHz, a configuration normally used for plasma etching. The infrared beam was restricted in such a way that the light passed only through the glow region of the plasma, where the electron density has its maximum value and therefore the excitation is maximal.

IV. RESULTS AND DISCUSSION

The plasma was operated at a pressure of 100 mTorr, 100 W rf power (which corresponds to about 0.6 W/cm²) and at several flows between 3 and 30 sccm CF₄. As a result of the presence of the plasma the relative intensities of the various Q branches changed considerably [see Fig. 2(b)]. A more or less systematic value of 2.35 (independent of the flow) was found for the ratio $I(Q_0)/I(Q_1)$, which shows that the vibrational temperature increases after the plasma has been switched on. The value of T_{vib} in the plasma corresponding to this ratio depends on the spatial distribution of T_{vib} (since the measurement only yields an average value over the line of sight of the infrared beam). To estimate this, a scan was made as a function of the radial position in the plasma. Unfortunately we were not able to measure beyond the edge of the electrodes, as a result of the shape of our vacuum (BaF₂) windows. In the electrode region however we found no substantial change of $I(Q_0)/I(Q_1)$ with the lateral position. This means that if we take T_{vib} to have a value higher than without plasma only in the electrode region (about half of the optical path through the vacuum vessel), we can determine an upper limit for T_{vib} . This value appears to be 400 ± 20 K, which is a relatively low value compared with the value of 3000 K reported from emission data of N₂ in CF₄ obtained by van Veldhuizen *et al.*⁷ In part this large difference can be explained by the fact that we used a rf power density about 3 times lower than they used. Furthermore the vibrational temperature of the electronically excited level of N₂ need not be equal to the T_{vib} of the ground level, since the upper level of N₂ may already be vibrational-

ly excited during the electronic excitation (as a result of the Franck–Condon principle). In our case we measure directly the vibrational temperature of the (electronic) ground state. It seems therefore that the plasma has but a small influence on the vibrational temperature of CF₄. To explain this we have to look at the excitation and deexcitation processes involved. Vibrational excitation can result from several processes. The first of these processes is vibrational excitation through inelastic collisions with electrons. The mean frequency τ_{exc}^{-1} of excitations of an CF₄ particle is given by

$$\tau_{\text{exc}}^{-1} = n_e \sigma_{\text{in}} v_e,$$

where n_e is the electron density, σ_{in} is the cross section for vibrational inelastic electron collision, and v_e is the mean electron speed given by

$$v_e = \left(\frac{2kT_e}{m_e} \right)^{0.5}.$$

The collision cross section σ_{in} has been calculated by Stefanov *et al.*¹³ who gives a value of about $7 \times 10^{-17} \text{ cm}^{-2}$. Taking $T_e = 5 \text{ eV}$ (which is a value commonly taken in the literature⁶) and $n_e = 1.3 \times 10^{10} \text{ cm}^{-3}$ (which has been measured in the same reactor¹⁴), we find that $\tau_{\text{exc}}^{-1} = 160 \text{ s}^{-1}$. A second possibility for the formation of vibrationally excited molecules is electron–ion recombination. In the case of CF₄, however, this process can be neglected since the CF₄⁺ ion is not stable and therefore too short lived to be able to recombine with an electron (in contrast to, e.g., N₂, where N₂⁺ is stable¹⁵ and could possibly give a contribution to the formation of vibrationally hot molecules). Finally vibrationally excited CF₄ molecules may be produced by sputtering of surface absorbed CF₄ as has been demonstrated for the case of SiO particles¹⁶ (from a Si surface in an O₂ plasma). In the case of CF₄, however, this process is negligible since the total number of ions impinging on the surface of the electrode per second (about 4×10^{17} , which can be calculated from the etch rate¹⁷ of SiO₂ and the sputter yield¹⁸ of SiO₂ by CF_x⁺ ions) is even lower than the number of CF₄ particles per second in the gas flow (about 8×10^{18} at 20 sccm). Therefore, in CF₄ direct excitation by collision with electrons is believed to be the main excitation mechanism for the creation of vibrationally excited CF₄ molecules. The main deexcitation process in this case is diffusion of the excited molecules to the wall and deexcitation on the wall. The diffusion frequency τ_{diff}^{-1} of the first mode of diffusion in a one-dimensional approximation is given by

$$\tau_{\text{diff}}^{-1} = \frac{\gamma D \pi^2}{d^2},$$

where d is the electrode separation, D is the self-diffusion constant for CF₄ (which is estimated to be $\sim 1000 \text{ cm}^2/\text{s}$ at 100 mTorr), and γ is the wall deexcitation coefficient. This gives us a value of $\gamma/4 \times 10^{-4} \text{ s}^{-1}$ which is therefore more than an order of magnitude faster than the excitation time constant if γ is close to 1. If this is so no high densities of vibrationally excited molecules can be built and T_{vib} has a value only slightly above room temperature. Since we found only a small increase of T_{vib} in the plasma, either the excitation coefficient of Stefanov *et al.*¹³ is overestimated, or γ is

indeed close to 1. Which of the two is the “true” explanation is difficult to say, but in any case the result is that vibrational excitation of CF₄ molecules in a capacitively coupled rf plasma is small.

From the shape of the R branch an estimate was drawn for the rotational temperature T_{rot} . We estimate a T_r of $350 \pm 10 \text{ K}$ for the plasma parameters used.

V. CONCLUSIONS

Measurements of the vibrational and rotational temperature in an 13.56 MHz rf CF₄ plasma were performed using infrared absorption spectroscopy. The results of the experiment indicate that the plasma has hardly any effect on the T_{vib} and T_{rot} of CF₄. We found only a small increase of T_{vib} and T_{rot} from room temperature to about 400 and 350 K, respectively, at 100 mTorr pressure and 0.6 W/cm² rf power density. The large difference of these measurements of the T_{vib} of CF₄ with respect to the T_{vib} of N₂ impurities in a CF₄ plasma⁷ may be a result of the difference in production mechanism. The results may also imply that only small effects are to be expected of the T_{vib} of CF₄ on the EEDF and rate coefficients in a CF₄ plasma and on the rate of formation of negative ions. This does however not exclude that other plasma species such as the dissociation products of CF₄ still can be vibrationally “hot.”

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