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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 $v_1$ 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 $v_1$ 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. A factor which can strongly affect the EEDF is the amount of vibrationally excited molecules, since the electrons can gain energy through superelastic collisions. 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 for 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.

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. 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 $v_2$ 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 $v_2$ transition will be significantly populated. This has an effect on the band shape of the $v_1$ peak. Besides the normal transition of $v_1$, which starts from the ground state, transitions are also possible from vibrationally excited states, such as $v_2$, $2v_2$, $3v_2$, etc. (see Fig. 1). The $Q$ branches with $\Delta J = 0$ of the transitions from these states will in the rest of this paper be denominated as $Q_1$, $Q_2$, $Q_3$, etc. Transitions from excited states are usually known as 'hot bands'. If the potential curve of CF₄ is harmonic the energy difference between the upper level $v_1 + n v_2$ and the lower level $n v_2$ 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 $v_3$ 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. Besides the 'normal' $v_3$ 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 $v_2$ levels relative to the ground state level. If we assume a Boltzmann distribution for the $v_2$ levels, the intensity ratio of $v_2' + v_1' - v_1'$ over $v_1'$ [or $I(Q')/I(Q_0)$] is equal to a Boltzmann factor exp($-h\nu_2/kT_{vib}$). Moreover, as a result of coupling of the two vibrations, the intensity of the

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm⁻¹)</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>908.5</td>
<td>1</td>
</tr>
<tr>
<td>$v_2$</td>
<td>435.0</td>
<td>2</td>
</tr>
<tr>
<td>$v_3$</td>
<td>1283.2</td>
<td>3</td>
</tr>
<tr>
<td>$v_4$</td>
<td>631.2</td>
<td>3</td>
</tr>
</tbody>
</table>
hot band transitions can also be slightly different from the intensity of the ground state transition. 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 take into account the intensity ratio for the Q bands can be written as

\[ \frac{I(Q_0)}{I(Q_n)} = C_n \frac{g_0}{g_n} \exp\left(-\frac{nh\nu_2}{kT_{\text{vib}}}\right), \]

where \( Q_n \) is the Q branch of \( \nu_3 \) starting from the \( n \)th level of \( \nu_2 \) (see Fig. 1), \( g_n \) is the statistical weight of the \( n \)th level, \( h \) Planck's constant, \( k \) 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 \( \nu_2 \) transition is doubly degenerated, the statistical weights \( g_n \) follow the series

\[ g_n = (1,2,3,\ldots). \]

For \( T_{\text{vib}} = 300 \) K and \( C_1 \) taken to be unity, this yields a value of 4.01 for \( \frac{I(Q_0)}{I(Q_1)} \). The measurement was calibrated by measuring \( \frac{I(Q_0)}{I(Q_1)} \) as a function of pressure (see Fig. 3). This resulted in a value of 3.27 for a measurement in CF\(_4\) 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 \( T_{\text{vib}} \) in the situation with plasma on from

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

To determine the rotational temperature in the plasma, a simulation of the shape of the R branch of the \( \nu_3 \) 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 by

\[ \nu(J) = \nu_0 + (1 - \xi_3) 2B_3 \]

where \( \nu_0 \) is the band center frequency, \( \xi_3 \) the Coriolis coupling factor for the \( \nu_3 \) transition and \( B_3 \) the rotational constant given by

\[ B_3 = \frac{\hbar}{8\pi^2cI_0}, \]

where \( \hbar \) is Planck's constant, \( c \) the speed of light, and \( I_0 \) the moment of inertia of CF\(_4\). The Coriolis coupling factor \( \xi_3 \) was taken from a measurement of the \( \nu_3 \) band at 0.03 cm\(^{-1}\) unapodized resolution and was found to be 0.81 in good agreement with literature values. The intensities of the ro-

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**Fig. 1.** Schematic representation of the vibrational transitions of CF\(_4\), 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 \( \nu_2 \) levels from which they start.

**Fig. 2.** High-resolution absorption spectrum of the CF\(_4\), \( \nu_3 \) 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 \( Q_0 \) = 0.5, whereas \( Q_1 \) is linear in the whole region investigated.
tional lines in the $R$ branch can be calculated from

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

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 arc 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 CF$_4$ 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 (similar to the one used by Jennings). 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 routine 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/cm$^2$) and at several flows between 3 and 30 sccm CF$_4$. 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 $I(Q_2)/I(Q_1)$, 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 (BaF$_2$) windows. In the electrode region however we found no substantial change of $I(Q_2)/I(Q_1)$ 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 N$_2$ in CF$_4$ obtained by van Veldhuizen et al. 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 N$_2$ need not be equal to the $T_{vib}$ of the ground level, since the upper level of N$_2$ 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 CF$_4$. 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 $\tau_{\text{exc}}^{-1}$ of excitations of an CF$_4$ particle is given by

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

where $n_e$ is the electron density, $\sigma_{\text{in}}$ 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 $\sigma_{\text{in}}$ has been calculated by Stefanov et al. who gives a value of about $7 \times 10^{-17}$ cm$^{-2}$. Taking $T_e = 5$ eV (which is a value commonly taken in the literature) and $n_e = 1.3 \times 10^{10}$ cm$^{-3}$ (which has been measured in the same reactor), we find that $\tau_{\text{exc}}^{-1} = 160$ s$^{-1}$. A second possibility for the formation of vibrationally excited molecules is electron-ion recombination. In the case of CF$_4$, however, this process can be neglected since the CF$_4^+$ ion is not stable and therefore too short lived to be able to recombine with an electron (in contrast to, e.g., N$_2$, where N$_2^+$ is stable and could possibly give a contribution to the formation of vibrationally hot molecules). Finally vibrationally excited CF$_4$ molecules may be produced by sputtering of surface absorbed CF$_4$ as has been demonstrated for the case of SiO$_2$ particles (from a Si surface in an O$_2$ plasma). In the case of CF$_4$, however, this process is negligible since the total number of ions impinging on the surface of the electrode per second (about $4 \times 10^{17}$) which can be calculated from the etch rate of SiO$_2$ and the sputter yield of SiO$_2$ by CF$_4^+$ ions) is even lower than the number of CF$_4$ particles per second in the gas flow (about $8 \times 10^{16}$ at 20 sccm). Therefore, in CF$_4$ direct excitation by a collision with electrons is believed to be the main excitation mechanism for the creation of vibrationally excited CF$_4$ 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 $\tau_{\text{diff}}^{-1}$ of the first mode of diffusion in a one-dimensional approximation is given by

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

where $d$ is the electrode separation, $D$ is the self-diffusion constant for CF$_4$ (which is estimated to be $\sim 1000$ cm$^2$/s at 100 mTorr), and $\gamma$ is the wall deexcitation coefficient. This gives us a value of $\gamma/4 \times 10^{-4}$ s$^{-1}$ which is therefore more than an order of magnitude faster than the excitation time constant if $\gamma$ is close to 1. If this is so high densities of vibrationally excited molecules can be built and $T_{\text{vib}}$ has a value only slightly above room temperature. Since we found only a small increase of $T_{\text{vib}}$ in the plasma, either the excitation coefficient of Stefanov et al. is overestimated, or $\gamma$ 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 CF$_4$ molecules in a capacitively coupled rf plasma is small.

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

V. Conclusions

Measurements of the vibrational and rotational temperature in an 13.56 MHz rf CF$_4$ plasma were performed using infrared absorption spectroscopy. The results of the experiment indicate that the plasma has hardly any effect on the $T_{\text{vib}}$ and $T_{\text{rot}}$ of CF$_4$. We found only a small increase of $T_{\text{vib}}$ and $T_{\text{rot}}$ from room temperature to about 400 and 350 K, respectively, at 100 mTorr and 0.6 W/cm$^2$ rf power density. The large difference of these measurements of the $T_{\text{vib}}$ of CF$_4$ with respect to the $T_{\text{vib}}$ of N$_2$ impurities in a CF$_4$ plasma 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 $T_{\text{vib}}$ of CF$_4$ on the EEDF and rate coefficients in a CF$_4$ 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 CF$_4$ still can be vibrationally "hot."

Acknowledgments

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