Vibrational excitation and relaxation of five polyatomic molecules in an electrical discharge

M. Eugenia Sanz, a Michael C. McCarthy, and Patrick Thaddeus
Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138 and Division of Engineering and Applied Sciences, 29 Oxford Street, Harvard University, Cambridge, Massachusetts 02138

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Vibrational excitation and relaxation of five linear polyatomic molecules, OCS, OC$_3$S, HC$_3$N, HC$_5$N, and SiC$_2$S, have been studied by Fourier transform microwave spectroscopy in a supersonic expansion after the application of a low-current dc electric discharge. For each chain, the populations in bending and stretching modes have been characterized as a function of the applied discharge current; for stable OCS and HC$_3$N, vibrational populations were studied as well in the absence of a discharge. With no discharge present the derived vibrational temperatures are slightly below $T$, the temperature of the gas before the supersonic expansion (i.e., 300 K). In the presence of the discharge, vibrational excitation occurs via inelastic collisions with the electrons and the vibrational temperatures rise as the applied current increases. Global vibrational relaxation is governed by rapid vibration–vibration (VV) energy transfer and slow vibration–translation (VT) energy transfer. The latter process is rate-determining and depends primarily on the wave number of the vibration. Vibrational modes with wave numbers near and below $kT/hc$ (where $T=300$ K and $kT/hc \sim 210$ cm$^{-1}$) are efficiently cooled by VT transfer because a sufficient number of collisions occur in the initial stages of the supersonic expansion. Vibrational modes with wave numbers around 450 cm$^{-1}$ appear to be inefficiently cooled in the molecular beam; at these energies VV and VT rates are probably comparable. For high-frequency vibrations, VV energy transfer dominates. For the longer chains OC$_3$S and HC$_5$N, higher-lying modes are generally not detectable and vibrational temperatures of most lower-lying modes were found to be lower than those of OCS and HC$_3$N, suggesting that as the size of the molecules increases, intermediate VV transfer becomes more efficient, plausibly due to the higher density of vibrational levels. New high resolution spectroscopic data have been obtained for several vibrationally excited states of OC$_3$S, HC$_3$N, and HC$_5$N. Rotational lines of the $^{13}$C and $^{15}$N isotopic species of HC$_5$N have been measured, yielding improved rotational and centrifugal distortion constants; $^{14}$N nitrogen quadrupole coupling constants for the isotopic species of HC$_5$N with $^{13}$C have been determined for the first time. © 2005 American Institute of Physics. [DOI: 10.1063/1.1869988]

I. INTRODUCTION

The effect of a supersonic expansion on molecular properties has been extensively studied, especially so with the advent of sensitive high resolution spectroscopic techniques. It is well known that the large number of collisions at the onset of the expansion produces very effective translational and rotational cooling, but incomplete vibrational cooling (see, for e.g., Ref. 1). Using molecular beam Fourier transform microwave spectroscopy (FTM) in combination with electric discharges, we have observed rotational transitions in vibrationally excited states of several radicals of astrophysical interest. In an attempt to better understand vibrational processes in our molecular beam discharge source, we have recently undertaken a systematic study of the rotational spectra of several diatomic and linear polyatomic molecules. For the diatomic molecules SO, SiO, and SiS, rotational transitions in vibrational states up to ~70% of the dissociation limit (0 ≤ $v$ ≤ 51) were detected. Two regions of vibrational excitation can be distinguished: the Treanor region for the lowest vibrational levels, characterized by a temperature around 1000 K, and a Plateau region for vibrational levels with $v > 4$, characterized by a temperature of a few thousand degrees Kelvin. These observations were explained in terms of slow vibration–translation (VT) energy transfer and rapid vibration–vibration (VV) energy transfer. Here we present an extension of these results to five linear polyatomic molecules: OCS, OC$_3$S, HC$_3$N, HC$_5$N, and SiC$_2$S.

Several studies of vibrational excitation of polyatomic molecules seeded in supersonic beams have been reported, including laser-induced fluorescence of aromatic hydrocarbons, electric resonance spectroscopy of OCS, HCN, and HC$_3$N, dispersed fluorescence spectroscopy of p-difluorobenzene, FTM studies of fluorobenzene, and millimeter-wave absorption spectroscopy of pyridine. These
studies have examined the effect of pressure, diluent gas, and type of vibrational motion (in-plane or out-of-plane) on the extent of vibrational cooling.

Discharges have also been used in combination with molecular beams to detect vibrationally excited states in polyatomic molecules. Grabow et al.\textsuperscript{10} showed that several excited vibrational states of OCS (up to 6200 cm$^{-1}$) and SO$_2$ (up to 2300 cm$^{-1}$) can be observed in a discharge in a molecular beam. More recently, Sutter and Dreizler\textsuperscript{11} have detected rotational transitions in the lowest vibrationally excited state of ketene (H$_2$CCO) in a pulsed discharge molecular beam source. Because a fairly small number of experiments have been performed to date, no systematic investigations of vibrational excitation in supersonic jet electric discharges have been undertaken so far, and no general trends which govern these processes have been spelled out.

In this paper we report a systematic study of the effect of an electric discharge on the vibrational excitation of five linear polyatomic molecules, OCS, OC$_3$S, HC$_3$N, HC$_5$N, and SiC$_2$S. OCS and HC$_3$N were chosen in part because their vibrational spectra have been extensively studied by infrared and rotational spectroscopy, and because they are stable molecules, so their vibrational distributions can be compared in the absence of the discharge and as a function of discharge current. OC$_3$S and HC$_5$N—the longer analogues of OCS and HC$_3$N—were also examined to better understand the effect of chain length and size on the degree of vibrational cooling. Vibrationally excited SiC$_2$S has also been studied in greater detail. A previous study of its rotational spectrum\textsuperscript{3} has been expanded here to quantify how a change in discharge current affects vibrational populations.

In the absence of an electrical discharge to provide energetic electrons, the vibrational temperature of OCS and HC$_3$N is approximately $T$, the temperature of the gas before the adiabatic expansion. When the discharge is applied, the vibrational temperatures of OCS and HC$_3$N increase roughly in proportion to the discharge current, as expected for collisional excitation by electrons. For OCS, rotational transitions from a total of eleven vibrational states (from the fundamental and overtones of the bending mode and the two stretching modes) have been detected with either neon or helium as the buffer gas. For OC$_3$S, transitions from the two highest-frequency bending modes, $v_b$ and $v_d$, have been detected, as has a strong progression in the $v_b$ mode [at $\sim 480$ cm$^{-1}$ (Ref. 12)] up to $v_b=4$. For HC$_3$N, a total of eight vibrational states which originate from all of the bending and stretching vibrations except $v_1$ (lying $3327$ cm$^{-1}$ above ground\textsuperscript{13}) have been observed. The most intense rotational transitions are from $v_b$ at $499$ cm$^{-1}$,\textsuperscript{13} a progression in $v_7$ to the third overtone has also been observed. For HC$_3$N, transitions from a total of eight vibrational levels, which all originate from the five lowest-frequency modes, $v_1$, through $v_7$, have been detected. The most intense lines are from $v_b$, lying $476.6$ cm$^{-1}$ above ground,\textsuperscript{14} and its overtones, up to $v_b=3$. For SiC$_2$S, the second lowest-frequency bending mode and the two highest-frequency stretching vibrations have been detected and assigned on the basis of recent high-level ab initio calculations.\textsuperscript{3} An intense progression in the second lowest-frequency bending mode, $v_4$ (lying approximately $480$ cm$^{-1}$ above ground\textsuperscript{13}) was observed up to $v_4=3$, which is qualitatively similar to that observed for OC$_3$S.

Our observations can be understood within the context of the schemes that Flynn,\textsuperscript{15} Orr and Smith,\textsuperscript{16} Clary et al.,\textsuperscript{17} and others\textsuperscript{18} proposed to explain collisionally induced vibrational energy transfer in small polyatomic molecules. VV energy transfer is very fast: rapid equilibrium of each vibrational mode within its manifold of levels is achieved by VV ladder-climbing (VV-lc) processes and near-equilibrium among different vibration modes via intermode VV (VV') processes, which are efficient when the energies of the different vibrational modes are similar. VT energy transfer is generally slow and is the rate-determining process in vibrational relaxation. We have found that VT energy exchange depends mainly on the wave number of the vibration.

For all of the polyatomic molecules studied here, vibrations with wave numbers at or below $kT/hc$ ($T$ the temperature of the gas before the supersonic expansion, 300 K, and $kT/hc \sim 210$ cm$^{-1}$) relax effectively to the ground state on the timescale of the expansion. VT transfer is efficient for these states because there is a sufficient number of collisions [typically $10^2$–$10^3$ (Ref. 1)] in the throat of the nozzle to cool them. The bottleneck for molecular vibrational relaxation seems to be VT transfer from the lowest-frequency vibrational mode above $kT$, which appears to be around 450 cm$^{-1}$ in our experiments. These modes, where VV and VT transfer rates are presumably comparable, do not relax on the time scale of the expansion, and therefore exhibit the most intense rotational satellite transitions. Relaxation of modes with wave numbers well above $kT/hc$ is dominated by VV processes and is difficult to predict, since it depends on complicated energy pathways specific for each molecule. However, the longer chains are generally characterized by lower vibrational temperatures, plausibly because of the more important role of VV' transfer due to the greater density of states for these species.

A by-product of the present investigation is new spectroscopic data for the five molecules studied here. More precise rotational and centrifugal distortion constants have been derived for the two highest-frequency stretching vibrations of HC$_3$N, $v_2=1$ and $v_3=1$, and nitrogen quadrupole coupling constants $eQq$ have been determined for the first time owing to the high resolution of Fourier transform microwave spec-

\begin{figure}[h]
\centering
\includegraphics{discharge_nozzle.png}
\caption{Cross section of the discharge nozzle used in our molecular beam Fourier transform microwave spectrometer.}
\end{figure}
been identified. For OC$_3$S, centimeter-wave transitions were
determined; the $^{14}$N-isotopic species were detected and refined rotational and cen-
tral transitions in the frequency ranges 8–18 GHz

A discharge is struck by applying a negative dc voltage
to one of the large mirrors of our Fabry–Pérot cavity and
measured for the two highest bending modes, $v_h$ and $v_s$. Several overtones of $v_s$ were also detected and their spectro-
copic constants determined to high precision.

II. EXPERIMENT

The molecular beam Fourier transform microwave spec-
trometer used in the present work has a pulsed discharge
source for the generation of unstable species. The discharge
nozzle (see Fig. 1) consists of a commercial solenoid valve
(General Valve, series 9) to which a Teflon™ housing is
attached. The Teflon housing is designed to fit in the center
of one of the large mirrors of our Fabry–Pérot cavity and
contains two copper electrodes separated by Teflon insula-
tors. A discharge is struck by applying a negative dc voltage
to one of the copper electrodes and grounding the other as
the gas expands through the nozzle.

Our present instrument operates from 5 to 43 GHz and
employs an axially oriented supersonic nozzle and a gate
valve which allows the small discharge source in the throat
of the nozzle to be readily serviced without breaking vac-
uum; in combination with computer control to provide
rapid data acquisition and analysis, it is now possible to
achieve nearly continuous operation over many tens of hours
or days.

Uniform experimental conditions were employed for the
measurements described here. These include: stagnation
pressure (2.5 kTorr), temperature (300 K), carrier gas (neon
or helium), nozzle diameter (1 mm), thicknesses of the elec-
trodes (0.19 and 0.32 cm), their diameter (0.305 and
0.498 cm) and separation (1 cm), repetition rate (6 Hz), mi-
crowave radiation pulse length (1 µs). For each molecule,
most measurements were repeated several times using ident-
tical experimental parameters (discharge voltage, microwave
power, etc.), to better estimate relative intensities. These pa-
rameters were chosen to optimize the intensity of the rota-
tional transitions in the vibrational ground state in each case.
On the assumption that the dipole moment changes little with
vibrational level, vibrational temperatures have been derived
to an accuracy of about 15%; this error is limited largely by
the reproducibility of the FTM intensities. Details of the pro-
duction conditions for each molecule are listed in Table I.
The vibrational states of each molecule that have been stud-
died along with their energies are summarized in Table II.

### Table I. Summary of present laboratory measurements

<table>
<thead>
<tr>
<th>Precursor gases</th>
<th>Carrier gases</th>
<th>Mol fraction (%)</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCS OCS</td>
<td>Ne</td>
<td>0.05</td>
<td>5,000,1000,1500</td>
</tr>
<tr>
<td>OCS OCS</td>
<td>He or Ne</td>
<td>0.08</td>
<td>5,000,1000,1500</td>
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<td>OC$_3$S O$_2$/HC$_3$H/CS$_2$</td>
<td>Ne</td>
<td>0.1/0.2/0.1</td>
<td>1200,1400,1600</td>
</tr>
<tr>
<td>HC$_5$N HC$_5$N</td>
<td>Ne</td>
<td>0.1</td>
<td>5,000,1000,1500</td>
</tr>
<tr>
<td>HC$_5$N HC$_5$N</td>
<td>Ne</td>
<td>0.1</td>
<td>1450</td>
</tr>
<tr>
<td>Si$_2$S SiH$_2$/HC$_3$H/CS$_2$</td>
<td>Ne</td>
<td>0.1/0.2/0.1</td>
<td>800,1200,1600</td>
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</table>

### Table II. Energies of the excited vibrational states studied.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>$E_{ vib}/hc$ (cm$^{-1}$)</th>
<th>Vibration</th>
<th>$E_{ vib}/hc$ (cm$^{-1}$)</th>
<th>Vibration</th>
<th>$E_{ vib}/hc$ (cm$^{-1}$)</th>
<th>Vibration</th>
<th>$E_{ vib}/hc$ (cm$^{-1}$)</th>
<th>Vibration</th>
<th>$E_{ vib}/hc$ (cm$^{-1}$)</th>
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<tr>
<td>$v_1 = 1$</td>
<td>859</td>
<td>$v_1^{11} = 1^{11}$</td>
<td>223</td>
<td>$v_1^{11} = 1^{11}$</td>
<td>109</td>
<td>$v_1^{11} = 1^{11}$</td>
<td>78</td>
<td>$v_1^{11} = 1^{11}$</td>
<td>115</td>
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<td>$v_1 = 2$</td>
<td>1711</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>446</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>263</td>
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<td>480</td>
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<td>$v_1 = 3$</td>
<td>2556</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>663.1</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>477</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>876</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>960</td>
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<td>$v_1 = 4$</td>
<td>3394</td>
<td>$v_1^{12} = 1^{12}$</td>
<td>499</td>
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<td>290</td>
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<td>1214</td>
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<td>$v_1^2 = 1^{11}$</td>
<td>521*</td>
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<td>663.2</td>
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<td>508</td>
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<tr>
<td>$v_1^2 = 1^{31}$</td>
<td>1574*</td>
<td>$v_1^2 = 1^{31}$</td>
<td>2079</td>
<td>$v_1^2 = 1^{31}$</td>
<td>642</td>
<td>$v_1^2 = 1^{31}$</td>
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<td>642</td>
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<tr>
<td>$v_1^2 = 1^{40}$</td>
<td>2105</td>
<td>$v_1^2 = 1^{40}$</td>
<td>2274</td>
<td>$v_1^2 = 1^{40}$</td>
<td>2274</td>
<td>$v_1^2 = 1^{40}$</td>
<td>2274</td>
<td>$v_1^2 = 1^{40}$</td>
<td>2274</td>
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<tr>
<td>$v_1 = 1$</td>
<td>2062</td>
<td>$v_2 = 1$</td>
<td>4101</td>
<td>$v_2 = 1$</td>
<td>6118</td>
<td>$v_2 = 1$</td>
<td>6118</td>
<td>$v_2 = 1$</td>
<td>6118</td>
</tr>
</tbody>
</table>

1 Energies from Ref. 42, except those marked with an asterisk, taken from Ref. 43.
2 Energies from Ref. 13.
3 Energies from Ref. 14, except $v_{10}$, taken from Ref. 29.
4 Energies from Ref. 34, except $v_{10}$, taken from Ref. 12.
5 Energies from Ref. 3.
6 $I$ is the quantum number associated to the vibrational angular momentum about the molecular axis.
TABLE III. Spectroscopic constants of the $v_2=1$ and $v_3=1$ stretching vibrations of HC$_3$N (in MHz).

<table>
<thead>
<tr>
<th>Constant</th>
<th>This work</th>
<th>Mallinson and Fayt (Ref. 13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>4527.494 89(16)$^a$</td>
<td>4527.530(31)$^b$</td>
</tr>
<tr>
<td>$D \times 10^3$</td>
<td>...</td>
<td>0.5384(51)</td>
</tr>
<tr>
<td>$eQq$</td>
<td>-4.235 5(32)</td>
<td>...</td>
</tr>
<tr>
<td>$\sigma^a$</td>
<td>1.3</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$1σ uncertainties (in parentheses) are in units of the last significant digit.

$^b$Calculated from Ref. 13 using the 1σ errors quoted and the conversion factor 1 cm$^{-1}$=29979.25 MHz.

$^c$rms deviation of the fit in kHz.

III. RESULTS AND ANALYSIS

A. New spectroscopic data

1. HC$_3$N

The rotational spectrum of HC$_3$N in vibrationally excited states has been extensively studied in the centimeter, millimeter-, and submillimeter-wave regions due to the chemical and astronomical importance of this molecule. Spectroscopic constants for all excited vibrational states, some of their combination bands, and Fermi resonance systems are well known. Molecular constants for the rare isotopic species have also been determined. Highly accurate spectroscopic data are available for the four lowest-energy vibrational modes (bending modes), while less accurate data are available for the three highest stretches.

Because the application of a dc electric discharge enables one to detect all of the HC$_3$N vibrational modes except for the highest stretch $v_1$ [at ~3327 cm$^{-1}$ (Ref. 13) above the ground vibrational state], rotational transitions in the $v_2$ and $v_3$ stretching vibrations [see Table I of Supplementary Material (SM), deposited in the Electronic Physics Auxiliary Publication Service (EPAPS) of the American Institute of Physics] can be measured very precisely in the centimeter band by the present technique. All the microwave transitions exhibit the expected $^{14}$N-quadrupole hyperfine structure. Analysis of the measured hyperfine components, using the standard Hamiltonian for a linear closed-shell molecule including quadrupole terms, yields improved rotational and centrifugal distortion constants and $eQq_0$ quadrupole coupling constants, which have been determined for $v_2$ and $v_3$ for the first time (see Table III).

2. HC$_5$N

The rotational and infrared spectra of HC$_5$N, the next member in the cyanopolyyne series (HC$_n$N, $n=1,3,5,\ldots$), have been studied by a number of research groups. The ground-state microwave spectra of the normal and all singly substituted isotopic species were initially investigated by Alexander et al., who also analyzed several rotational satellites which correspond to the $v_1$ and $v_10$ vibration modes. Spectroscopic constants for the ground vibrational state were later improved and rotational spectra of the bending modes $v_{11}=1-9$, $v_{10}=1-3$, $v_9=1,2$, $v_8=1, v_7=1$, and the combination band ($v_{11}=1, v_{10}=1$) have been measured and analyzed. Less work has been done on the infrared spectra of this molecule: only the $v_1$ and $v_2$ band systems have been studied.

Although studies of the rotational spectrum of HC$_5$N were not the original aim of this work, its transitions are readily detected in our discharge under a number of different experimental conditions and with several precursor gases. On the basis of the spectroscopic constants given in Ref. 19, direct $l$-type microwave transitions in the lowest vibrationally excited states—the five doubly degenerate bending vibrations $v_11$, $v_10$, $v_9$, $v_8$, and $v_7$—were detected. Transitions from the lowest-frequency bending vibration $v_{11}$ ($\sim$108 cm$^{-1}$) were extremely weak in comparison with those from the other excited vibrational states. In contrast, a strong progression of $v_9$ ($\sim$477 cm$^{-1}$) up to the third quanta was observed, as was the overtone $v_7=2$ of the highest-frequency bend ($v_7 \sim$642 cm$^{-1}$). Lines assigned to the $v_9$ and $v_7$ overtones appear at approximately twice or three times the frequency difference between the ground state and the respective fundamental (see Fig. 2). Only N-nuclear quadrupole coupling hyperfine structure was observed in the rotational spectra arising from $v_7=2$, $v_9=2$, and $v_9=3$, indicating that the $l$-type doubling for these vibrational states is unresolved at our instrumental resolution of 5 kHz. The measured transitions (see Tables II and III of SM) were analyzed using the standard Hamiltonian for a linear molecule including the necessary terms to take into account the $l$-type doubling. The

FIG. 2. Stick spectrum of the $J=8 \rightarrow 7$ transition of HC$_3$N, showing the relative intensity of this rotational transition in the observed vibrationally excited states.
isotopic species were determined for the first time in the course of our investigations \(^{26}\) and they are in very good agreement with the available experimental values provided that the excited vibrational states are not perturbed. On the basis of these calculations, dedicated searches for the rotational satellites of the high-frequency stretching modes of HC\(_5\)N have been undertaken. Unfortunately, no lines that could be attributed to these modes were observed, indicating that these modes, with energies approximately in the range 600–3500 cm\(^{-1}\) (Ref. 14) are not sufficiently populated in our molecular beam.

Microwave transitions of the singly substituted \(^{13}\)C and \(^{15}\)N isotopic species of HC\(_5\)N were also observed in natural abundance in the course of our investigations (see Tables IV and V of SM\(^{23}\)). From the analysis of the measured transitions, improved rotational and centrifugal distortion constants—more accurate by one to two orders of magnitude than those reported in Ref. 24—were derived (see Table V). The nitrogen quadrupole coupling constants \(eQq\) for the \(^{13}\)C isotopic species were determined for the first time (see Table V).

### 3. OC\(_3\)S

Spectroscopic constants for all of the vibrationally excited states of OC\(_3\)S have been derived from studies of its millimeter-wave and infrared spectra.\(^{12,31–34}\) In the work here, only the bending vibrations \(v_6\sim438\) cm\(^{-1}\) and \(v_5\sim544\) cm\(^{-1}\) were detected. No lines from the lowest-frequency bending mode \(v_5\sim78\) cm\(^{-1}\) were observed despite long integrations. We also found no evidence of lines from any of the stretching vibrations despite dedicated searches, suggesting that these modes are poorly populated following the adiabatic expansion.

Lines in the second lowest-frequency bending mode, \(v_6\), were so strong that overtones up to \(v_6=4\) were identified. Their spectroscopic constants derived after fitting the standard Hamiltonian for a linear molecule to the measured transitions (Table VI of SM\(^{23}\)) are given in Table VI.

### B. Vibrational relaxation

#### 1. General model: OCS and HC\(_5\)N

Because OCS and HC\(_5\)N are stable molecules, their vibrational excitation and relaxation can be investigated in the absence of the dc electric discharge and as a function of voltage and current in contrast to unstable species that are only produced by a discharge (see Table I). The lowest two rotational transitions \((J=1\rightarrow0\) and \(2\rightarrow1\)) of OCS were studied in different vibrationally excited states with either Ne or He as buffer gases, as was the \(J=2\rightarrow1\) transition of HC\(_5\)N in Ne. The vibrational temperature of each mode was determined by fitting the relative intensities of the rotational transitions arising from the different vibrational levels with respect to the ground vibrational state on the assumption of Boltzmann distribution. When only the fundamental of an excited vibrational state was detected, its temperature was derived from the standard expression

\[
\ln \frac{I(v_i)}{I_0} = -\frac{hcG_{v_i}}{k} \frac{1}{T_{v_i}},
\]

where \((v_i)\) and \(I_0\) are the intensities of the rotational transitions in the \(v_i=1\) vibrational state and the ground vibrational state, respectively, and \(G_{v_i}\) is the energy of the \(v_i=1\) state.

In the absence of an electric discharge only the lowest few excited vibrational states are populated after the supersonic expansion (see Tables VII and VIII). For OCS the first two quanta of the bending mode \((v_6)\) and the first quantum of the lowest stretching mode \((v_7)\) are observed; for HC\(_5\)N the first quanta of the three degenerate bends \((v_5, v_6, v_7)\) and the
lowest stretch ($\nu_4$) are detected, along with the second overtone of the lowest-frequency bending mode ($\nu_7=2$). All of the vibrations of both molecules have effective temperatures slightly below $T$ ($T$ being room temperature for our experiments) except the lowest bending mode $\nu_7$ at 223 $\text{cm}^{-1}$, whose temperature is 88±1 K, considerably lower than $T$.

In the presence of the dc electric discharge, additional vibrational modes (and their overtones) can be detected in our molecular beam. Both the number of vibrational modes and their temperatures generally increase with the increase in discharge current. Vibrational temperatures are typically higher than $T$ (see Tables VII and VIII), and stretching modes are in general hotter than bending vibrations, especially for OCS. It is worth noting that the temperature of the lowest-frequency bend of HC$_3$N, $\nu_7$, with an energy comparable to $kT$ ($T$~300 K, $kT$~210 $\text{cm}^{-1}$), only increases by ~30% (to 114±7 K, a value well below $T$) with the application of a 500 V (10 mA) discharge, while the temperature of the second lowest-frequency bend doubles (from 224 to 446 K, see Table VIII).

As the discharge current increases beyond a certain value, typically ~1500 V in our experiments, the signal-to-noise ratio of the OCS and HC$_3$N lines steadily decreases, as expected if the rate of molecular vibrational excitation by collisions with electrons is eventually overcome by fragmentation. Vibrational temperature diagrams for OCS and HC$_3$N are displayed in Figs. 3 and 4.

The mechanisms for vibrational excitation and relaxation which are operative in collisionally-induced vibrational energy transfer$^{15,17}$ provide a good framework to understand our observations. Prior to expansion, molecules have a room temperature vibrational distribution. In the absence of the discharge, vibrations simply relax during the supersonic expansion via collisional VT energy transfer with the rotationally cold, but translationally hot buffer gas and via VV energy transfer with other molecules present in the molecular beam. Application of the dc electric discharge introduces a very energetic source of electrons, which rapidly excite molecular vibrations via inelastic collisions. Energy enters the molecule via VT transfers from $\nu=0$ to $\nu=1$ of the different vibration modes, where the largest VT cross sections usually involve the lowest-frequency vibrational mode because the

### TABLE VI. Spectroscopic constants for the overtones of the $\nu_4$ bending vibration of OC$_3$S (in MHz).

<table>
<thead>
<tr>
<th></th>
<th>$\nu_4=2^{0^a}$</th>
<th>$\nu_4=2^{2}$</th>
<th>$\nu_4=3^{1,3}$</th>
<th>$\nu_4=4^{0,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>1417.843 67(19)$^b$</td>
<td>1418.012 60(22)</td>
<td>1420.025 03(22)</td>
<td>1422.011 75(27)</td>
</tr>
<tr>
<td>$D \times 10^4$</td>
<td>0.045 2(20)</td>
<td>0.045 9(22)</td>
<td>0.046 7(22)</td>
<td>0.046 1(27)</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$ is the quantum number associated with the vibrational angular momentum about the molecular axis.

$^b$ 1σ uncertainties (in parentheses) are in units of the last significant digit.

### TABLE VII. Effective vibrational temperatures for the different excited states of OCS.

<table>
<thead>
<tr>
<th>$V$ (V)</th>
<th>$\nu_2$ Bending mode</th>
<th>$\nu_1$ Lowest stretching mode</th>
<th>$\nu_3$ Highest stretching mode</th>
<th>$I$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas He, $J=1\rightarrow0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>263±2$^a$</td>
<td>⋯</td>
<td>⋯</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>285±7</td>
<td>307±12</td>
<td>1013±70</td>
<td>1</td>
</tr>
<tr>
<td>1000</td>
<td>629±71</td>
<td>545±9</td>
<td>1502±69</td>
<td>12</td>
</tr>
<tr>
<td>1500</td>
<td>909±239</td>
<td>694±114</td>
<td>2460±232</td>
<td>40</td>
</tr>
<tr>
<td>Carrier gas He, $J=2\rightarrow1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>197±2</td>
<td>253±1</td>
<td>⋯</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>289±56</td>
<td>303±9</td>
<td>850±28</td>
<td>1</td>
</tr>
<tr>
<td>1000</td>
<td>412±63</td>
<td>458±4</td>
<td>1402±100</td>
<td>12</td>
</tr>
<tr>
<td>1500</td>
<td>625±23</td>
<td>922±91</td>
<td>2773±317</td>
<td>40</td>
</tr>
<tr>
<td>Carrier gas Ne, $J=1\rightarrow0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>196±1</td>
<td>279±5</td>
<td>⋯</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>326±59</td>
<td>469±47</td>
<td>917±32</td>
<td>4</td>
</tr>
<tr>
<td>1000</td>
<td>787±227</td>
<td>1491±102</td>
<td>1757±89</td>
<td>30</td>
</tr>
<tr>
<td>1500</td>
<td>833±39</td>
<td>1530±147</td>
<td>2919±331</td>
<td>80</td>
</tr>
<tr>
<td>Carrier gas Ne, $J=2\rightarrow1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>190±20</td>
<td>277±1</td>
<td>⋯</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>325±18</td>
<td>503±71</td>
<td>909±25</td>
<td>4</td>
</tr>
<tr>
<td>1000</td>
<td>606±254</td>
<td>1162±36</td>
<td>1405±145</td>
<td>30</td>
</tr>
<tr>
<td>1500</td>
<td>794±68</td>
<td>1724±167</td>
<td>2482±59</td>
<td>80</td>
</tr>
</tbody>
</table>

$^a$ 1σ uncertainties.
energy difference is the smallest. Population in $v=1$ is then rapidly redistributed to higher vibrational energy levels via VV energy transfers, which can take place within the same vibrational mode (VV ladder-climbing or VV-lc, which is the VV transfer mechanisim in diatomics) or among different vibrations (intermode VV transfer or VV'). VV-lc is generally faster than VV' because the energy differences are usually very small.

Vibrational relaxation happens through the reverse process. For a polyatomic molecule, VV processes give rise to a situation where the different vibrational modes are in near-equilibrium with each other. The overall vibrational energy usually relaxes via a single-step rate-determining VT process, which normally involves the lowest vibrational mode.\(^1\)\(^5\),\(^3\)\(^5\)

The probability of VT energy transfer in a binary collision, assuming that SSH theory is qualitatively valid,\(^3\)\(^5\) depends inversely on the vibrational wave number; it is also affected by the amplitude of the vibration, the collision effectiveness (dependent on the vibrational mode), and the shape of the intermolecular potential. Empirically we find that the wave number of the vibration is the main factor affecting VT energy exchange. VT energy transfer is the dominant mechanism for relaxation of high-frequency vibrations, because VT transfer is extremely slow for them, and because these modes may more readily undergo VV' transfer owing to the higher density of vibrational modes. For vibrations with intermediate wave numbers, VV and VT energy transfers are probably comparable.

VT energy transfer in our expansion is apparently efficient for those modes whose vibrational wave numbers are lower or of order $kT/hc \ (\sim 210 \text{ cm}^{-1} \ in \ our \ experiment)$, presumably because a sufficient number of binary collisions—typically $10^2 \sim 10^5$ (Ref. 1)—occur in the throat of the nozzle. This result is supported by several observations: the three vibration modes of OCS have wave numbers well above $kT/hc$ (see Table II), and all are characterized by vibrational temperatures near or above $T$, implying that VT transfer is not efficient; for HC$_3$N, the lowest vibrational mode $v_7$, with an energy very close to $kT/hc$ (223 cm$^{-1}$,\(^1\)\(^3\)) see Table II), has a temperature well below $T$, indicating partial relaxation.

The effect of VT energy transfer in HC$_3$N is more noticeable in the presence of the discharge: all of the other HC$_3$N vibrational temperatures raise considerably as a consequence of the increased amount of vibrational energy in the molecule, but $T_{v_7}$ increases only by 30% (Table VIII). Because $v_7$ partially relaxes, the bottleneck process for the overall vibrational relaxation is the VT energy transfer from the first vibrational level of the second-lowest frequency vibration, $v_6=1$ at 499 cm$^{-1}$ (Ref. 13) to the ground vibrational state. This mode appears to be effectively excited in the molecular beam (see Fig. 4), and its rotational lines are intense—considerably more intense than those from $v_7=2$, lying at almost the same energy. Similar behavior of HC$_3$N in molecular beams was observed by DeLeon and Muenter,\(^6\),\(^3\)\(^6\) who reported significant vibrational cooling for the $v_7$ vibration and the same intensity ordering observed here for the lowest bending modes, i.e., $v_6 > v_7 > v_5$.

Vibrationally excited OCS diluted in either He or Ne has been studied. The vibrational temperatures derived for each

<table>
<thead>
<tr>
<th>V (V)</th>
<th>$v_7$</th>
<th>$v_6$</th>
<th>$v_5$</th>
<th>$v_4$</th>
<th>$v_3$</th>
<th>$v_2$</th>
<th>$I$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88±1(^a)</td>
<td>224±17</td>
<td>159±8</td>
<td>181±3</td>
<td>···</td>
<td>···</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>114±7</td>
<td>446±26</td>
<td>228±11</td>
<td>319±12</td>
<td>838±12</td>
<td>599±10</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>81±1</td>
<td>427±166</td>
<td>392±116</td>
<td>804±214</td>
<td>84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>···</td>
<td>···</td>
<td>···</td>
<td>···</td>
<td>···</td>
<td>···</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\)Uncertainties.


FIG. 3. Temperature diagrams for OCS in Ne at (a) 500 V, and (b) 1500 V. Vibrational temperature uncertainties are displayed in Table VII.

\(\text{OCS in Ne} \quad \text{HV} = 500 \text{ V, } I = 4 \text{ mA} \quad J = 2 \rightarrow 1\)

\(\text{OCS in Ne} \quad \text{HV} = 1500 \text{ V, } I = 80 \text{ mA} \quad J = 2 \rightarrow 1\)
vibrational mode with either buffer gas are not significantly different at similar currents (see Table VII), in agreement with previous observations. However, the vibrationally excited states of OCS are more populated with respect to the ground state when Ne is used in the expansion, as shown in Fig. 5. At a current of 30 mA, the bending mode and the lowest stretch appear to be more populated than \( v=0 \), and the highest stretch has a population comparable to that of the ground state. This distribution might be caused by the higher electron temperatures that can be reached with Ne,\(^3\) which produces more energetic vibrational excitation, and might even lead to population inversion if VT transfer is not efficient.

2. Longer chains

The three other linear molecules investigated here, OC\(_3\)S, HC\(_5\)N, and SiC\(_2\)S, were all produced with a dc electric discharge using different precursor gases. As before, the vibrational distribution of each was studied as a function of discharge current with the upper limit of the current determined by production requirements. Vibrational temperatures of each molecule generally follow the same trend as that observed here for OCS and HC\(_3\)N: the temperatures increase with current.

For HC\(_3\)N, all bending vibrations have been detected in a 1450 V (19 mA) discharge (see Fig. 2); their vibrational temperatures are summarized in Table IX. The lowest vibrational mode \( \nu_{11} \) of HC\(_3\)N lies at \( \sim 109 \text{ cm}^{-1} \) (Ref. 14)—considerably below \( kT/\hbar c \sim 210 \text{ cm}^{-1} \)—and, as expected, is very efficiently cooled in the molecular beam to about 25 K (see Table IX). Rotational lines arising from this vibration are extremely weak in comparison with those from other vibrations, and could only be detected here because of the high abundance of HC\(_3\)N in our discharge.

A relatively low temperature (\( \sim 110 \text{ K} \), see Table IX) has been also derived for the second lowest-frequency vibration, \( \nu_{10} \) (at 263 cm\(^{-1} \), see Table II), which suggests that it undergoes some relaxation in the supersonic expansion. As before, this result can be explained via the combination of partially effective VT transfer (since the vibrational wave number of \( \nu_{10} \) is only slightly above \( kT/\hbar c \)) and VV exchange. If VT transfer is only somewhat efficient in relaxing \( \nu_{10} \), then it should be even less efficient for the \( \nu_9 \) bending vibration of HC\(_3\)N, which has a vibrational wave number of \( \sim 477 \text{ cm}^{-1} \). Not surprisingly, this mode is efficiently excited in our expansion; its temperature (around 260 K) is twice that of \( \nu_{10} \) and a very strong progression up to the third overtone has been observed.

Vibrational temperatures of HC\(_5\)N are generally lower than those of HC\(_3\)N. Because the density of modes is higher in HC\(_5\)N, VV' transfer may play a more important role in vibrational relaxation, allowing vibrational energy to dissipate more readily in larger molecules.

Similar behavior to that of HC\(_3\)N has been observed for OC\(_3\)S and SiC\(_2\)S. The lowest vibrations of both molecules are well below \( kT/\hbar c \) (see Table II), and neither could be detected in the molecular beam, indicating efficient relaxation via VT processes. The second-lowest frequency modes of both molecules are considerably more intense, with several quanta populated in the beam, and their derived vibrational temperatures are also noticeably higher than those of the other vibrations. These modes are well populated because of the slow VT transfer to the ground vibrational state. For the molecules studied here, this effect is important for vibrational modes with wave numbers around 450 cm\(^{-1}\).

For OC\(_3\)S, only one vibration (\( \nu_5 \)) apart from the second lowest-frequency bend has been detected. Although more experimental data will be necessary to compare properly the

### Table IX. Effective vibrational temperatures for the different excited states of HC\(_3\)N\(^4\)

<table>
<thead>
<tr>
<th>( J' \rightarrow J'' )</th>
<th>( \nu_{11} )</th>
<th>( \nu_{10} )</th>
<th>( \nu_9 )</th>
<th>( \nu_8 )</th>
<th>( \nu_7 )</th>
<th>( \nu_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 ( \rightarrow ) 5</td>
<td>24(^{+1}) ( \pm 1 )</td>
<td>108( \pm 7 )</td>
<td>250( \pm 24 )</td>
<td>193( \pm 11 )</td>
<td>111( \pm 7 )</td>
<td>269( \pm 29 )</td>
</tr>
<tr>
<td>7 ( \rightarrow ) 6</td>
<td>24( \pm 1 )</td>
<td>138( \pm 11 )</td>
<td>244( \pm 3 )</td>
<td>226( \pm 15 )</td>
<td>329( \pm 38 )</td>
<td></td>
</tr>
</tbody>
</table>

\(^4\) All measurements done at a voltage of 1450 V (current of 75 mA).

\(^{+1}\) \( \nu_7 \) uncertainties.

---

FIG. 4. Temperature diagram for OC\(_3\)S at 1000 V. Vibrational temperature uncertainties are displayed in Table VII.

FIG. 5. Temperature diagram for OCS at 1000 V. Vibrational temperature uncertainties are displayed in Table VII.
vibrational temperatures of the OC$_3$S vibrations with those of OCS, the temperature calculated for $v_5$ is notably lower than the vibrational temperatures obtained at similar currents for OCS (see Tables VII and X), which is consistent with more efficient relaxation plausibly owing to a higher density of states and more effective VV$^\prime$ transfer for longer chains.

SiC$_2$S was studied at three different voltages (currents) by monitoring its strongest microwave transition, $J=4\rightarrow3$, near 13 GHz (see Table XI). Even with exhaustive searches guided by $ab$ initio calculations, no lines were detected from the lowest stretching vibration $v_5$. The small energy gap between $v_4$ and $v_3$ (predicted $ab$ initio to be 53 cm$^{-1}$) might allow near-resonant VV$^\prime$ transfers between these two vibrations, and might efficiently relax $v_3$. Unfortunately, no detailed information can be extracted from our present data about the preferential pathways for vibrational relaxation for this molecule.

**IV. DISCUSSION**

A limit of about $kT/hc$ (being $T=300$ K in our experiment, $kT/hc \sim 210$ cm$^{-1}$) has been established for effective VT transfer in our discharge from the derived vibrational temperatures of the lowest few excited vibrational states of the molecules studied (see Fig. 6). This limit is consistent with other observations of excited vibrational states by FTM spectroscopy. Schäfer and Bauder detected rotational transitions from four excited vibrational states of fluorobenzene and estimated their vibrational temperatures. They found that the lowest-frequency mode, at 248.6 cm$^{-1}$, had the lowest temperature ($65–70$ K), while the second lowest-frequency mode, at 400.4 cm$^{-1}$, had the highest temperature ($\sim 140$ K). The other two modes, at 413.9 and 517.1 cm$^{-1}$, had temperatures of 130 and 100 K, respectively. In an experiment similar to ours, Sutter and Dreizler observed rotational lines from the lowest vibrationally excited state of ketene (439 cm$^{-1}$) to be only four times less intense that those from the ground state, indicating fairly efficient excitation. However, no signals of other low-lying bending vibrations (at wave numbers of 528 and 587 cm$^{-1}$) were detected.

Studies of I$_2$ diluted in different gases have shown that vibrational relaxation is more efficient when the buffer gas is not monatomic, but instead a diatomic or a polyatomic molecule. This result is also in agreement with our observations, because VV transfer rates will be enhanced by the increase in the possible number of near resonances between vibrational states. Another factor that is believed to enhance vibrational relaxation, the formation of van der Waals complexes, will also be more important when heavier diluents are used.

The vibrationally excited levels in our discharge appear generally to be populated according to a Boltzmann distribution. This may be because VV$\rightarrow$c$c$ connects the manifold of levels of a vibration very quickly, so that each mode is characterized by its own vibrational temperature. Deviations from a Boltzmann distribution exist however for the highest overtones of some of the vibrations. Specifically, $v_4=3$ of SiC$_2$S at 1600 V has a higher population than expected; the same behavior was also observed for $v_3=3$ of HC$_3$N at 1450 V in its three rotational transitions, and for the fourth overtone of the lowest stretch of OCS in Ne at 500 V (see Fig. 3). Although it is difficult to establish how vibrational energy flows in each molecule, these deviations might arise because of near resonances between vibrations, which can enhance or direct population preferentially to one of the near-resonant levels via VV$^\prime$ transfer, and are more likely to occur at higher energies, where more states from overtones or combination bands can be reached.

The increase in the size of the molecule has been found to produce a decrease in the effective vibrational temperatures, an effect which is most noticeable on comparing HC$_3$N and HC$_5$N. It would be interesting to extend the present measurements to much longer cyanopolyyynes, up to HC$_{11}$N, for example. The $^{13}$C isotopic species of these longer chains have already been detected in natural abundance in our molecular beam, so rotational transitions from vibration...
tionally excited states even 100 times less intense than the ground vibrational state may be observable. To this end, reliable ab initio calculations of the cubic force field are desirable to determine vibration–rotation coupling constants and \( l \)-type doubling constants.

The threshold for effective VT transfer is determined by the number of collisions in the early stages of the adiabatic expansion. Because the number of collisions depends on the background pressure and the nozzle diameter, it may be worthwhile to conduct further experiments in which these parameters are varied to better understand how the resulting vibrational temperatures and the overall vibrational relaxation change.

To summarize, through the study of five polyatomic molecules we have found that VT transfer is the rate-determining process for vibrational excitation and relaxation and that it primarily depends on the inverse of the vibrational wave number, \( \sim kT/\hbar c \) being the limit for efficient VT transfer in our experimental conditions. In addition, we have obtained new spectroscopic data on the vibrationally excited states of HC\(_3\)N, HC\(_5\)N, and OC\(_3\)S. Rotational transitions of the isotopic species with \( ^{13}\text{C} \) of HC\(_3\)N have also been measured and their quadrupole coupling constants have been first determined in this work. More accurate rotational constants have also been derived for the \( ^{13}\text{C} \) and the \( ^{15}\text{N} \) isotopomers of HC\(_3\)N.

The use of electric discharges in combination with FTM spectroscopy is a very efficient technique to study vibrationally excited molecules. A heatable nozzle has also been employed to populate higher-lying vibrational levels as the temperature of the nozzle was raised (see, e.g., Ref. 41). Because vibrational excitation is determined by inelastic molecular collisions with electrons, at temperatures typically of \( \sim 10^5 \) K, use of an electric discharge is likely to populate higher vibrational excited states than a heated nozzle, which will enable the study of vibrationally excited states previously thought to be unobservable in a molecular beam experiment.

ACKNOWLEDGMENTS

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23See EPAPS Document No. E-JCPSA6-122-011514 for Tables I–VI. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.