ROTATIONALLY RESOLVED SPECTROSCOPY OF TETRACENE AND

ITS VAN DER WAALS COMPLEXES WITH INERT GAS ATOMS

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Rovibronic spectra of tetracene ($C_{18}H_{12}$) and its Van
der Waals complexes with argon and krypton have been
resolved by using a well collimated molecular beam
in combination with a single frequency dye laser. The
rotational constants of tetracene have been deduced
in the S_0 and S_1 electronic state. The rovibronic
spectra of the Van der Waals complexes show an en-
hanced *intersystem crossing*.

1. INTRODUCTION

During the last decade there has been an increasing
interest in the study of large molecules and their van der
Waals (VdW) complexes. Part of this interest is caused by the
development of very sensitive laser-spectroscopic techniques
in combination with effective reduction of the internal
energy of such molecules in molecular beams. Most of these
experiments use a free jet expansion in which the laser beam
crosses the molecular beam very near the nozzle. For large
aromatic molecules like anthracene or tetracene this allows
vibrational resolution and provides a tool for the study of
processes like intermolecular vibrational relaxation and

intersystem crossing[1].

The rotational spectra of such large molecules can be resolved by strongly collimating the molecular beam, thus decreasing the residual Dopplerwidth. This provides a very high resolution and allows the study of for instance the fluorene-argon VdW complex[2] or even the revelation of the molecular eigenstates of pyrazine[3].

Now we report the first observation of rotationally resolved spectra of tetracene (T) and its VdW complexes with argon and krypton. The T molecule and its VdW complexes have been studied under vibrational resolution[1,4,5] and calculations have been reported on the structure of the T-Ar complex[6]. An enhanced intersystem crossing in the complex has been concluded from lifetime measurements on the T-rare gas complexes[4]. We affirm this perturbation of the S_1 electronic state from our spectroscopic data of T-Ar and T-Kr. Besides we report the analysis of the rovibronic spectra of T from which we deduced molecular constants of this molecule in the S_0 and S_1 electronic state. All strong spectral features could be assigned and we found no evidence for perturbations of the S_1 state like have been observed for pyrazine[3] or are present in the T-rare gas complexes.

2. <u>EXPERIMENTAL</u>

In our studies we used the seeded beam technique, combining the advantage of a considerable reduction of the internal temperature of the molecules with a high density of VdW complexes. In molecules as large as T, such internal cooling is indispensable for reduction of the numerous spectral lines. The experimental set-up has been described in

detail before[7,8]. We used a quartz source in which a supply
of T was heated to $210\,^{\circ}$C, mixed with a noble gas and expanded
in a vacuum chamber by a nozzle (100 μm diameter). The mole-
cular beam was doubly skimmed to decrease the residual
Doppler width to about 15 MHz in the interaction zone with
the radiation field. The undispersed laser induced fluores-
cence was imaged to the photocathode of a PMT (EMI 9863/350
QA), monitored by a standard photon-counting system with an
integration time of typically 0.1 sec.

     We obtained the narrow band radiation field from a
standard dye laser system (Coherent 599-21) with a 3 MHz
bandwidth and a maximum output power of 50 mW. The bandwidth
however could be increased to about 30 GHz by removing the
intracavity etalons, thus allowing continuous laser scans
(by tuning a Lyot filter) over the whole region of the gain
medium.

     For relative frequency marking we used a sealed off
temperature stabilized Fabry-Perot interferometer with a
150 MHz free spectral range. Absolute frequency measurements
have been performed with a home-built Michelson interfero-
meter-type wavelength meter[8].

3. RESULTS AND DISCUSSION

3.1. $S_0 \rightarrow S_1$ transition in tetracene

     The $S_0 \rightarrow S_1$ electronic transition in tetracene was
studied by Amirav et al under vibrational resolution[1].
Several vibrational levels were assigned in both the S_0 and
S_1 state. At vibrational energies below $E_v = 1000$ cm^{-1} iso-
lated levels were observed while above this level Fermi reso-
nances appear, fading into a quasi continuum at $E_v = 1900$ cm^{-1}.
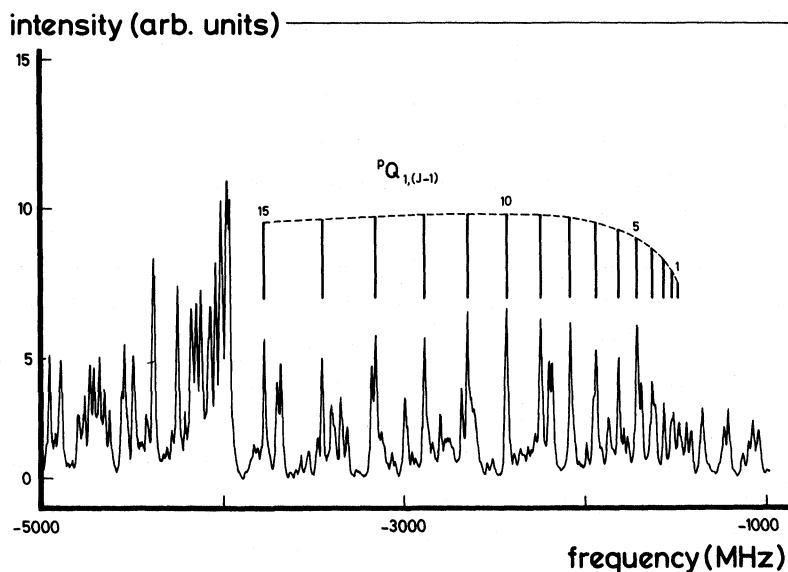
FIGURE 1   Part of the $S_0 \rightarrow S_1$ rovibronic transition of tetra-
cene at 22396.53(2) cm^{-1}. The indicated lines be-
long to a Q-branch with $\Delta k_{-1} = -1$, $k_{-1} = 1$ and
$k_1 = J - 1$.

We studied three vibronic transitions in the low energy range
(below $E_v = 1000 \ cm^{-1}$) under rotational resolution (table 1).
Two of these vibrations are totally symmetric a_g-type
vibrational modes, which are active for the $S_0 \ (^1A_g) \rightarrow$
$S_1 (^1B_{2u})$ symmetry allowed electronic transition. We also in-
vestigated a non-totally symmetric vibration of b_{3g} type.
Transitions to this vibrational mode gain their intensity
from a coupling with the higher energy $^1B_{1u}$ electronic state
and are of much less intensity as the symmetry allowed
transitions.

The observed spectrum around 22397 cm^{-1} was identified
by Amirav et al. as the electronic origin of the $S_0 (^1A_g) \rightarrow$

TABLE 1   Excited state vibrational assignments and experi-
           mental transition frequencies of tetracene and the
           redshifts of transitions in the T-Ar and T-Kr VdW
           complexes

T			T-Ar	T-Kr
$\nu_0 (cm^{-1})$	assignment	symmetry	$\Delta\nu_0 (cm^{-1})^{a)}$	$\Delta\nu_0 (cm^{-1})^{a)}$
22 396.53(2)	electronic origin	a_g	41.67(5)	66.9(1)
22 707.84(2)	311 cm^{-1}	a_g	41.41(5)	66.5(1)
22 876.62(2)	471 cm^{-1}	b_{3g}	41.47(5)	

[a] The accuracy is limited by the lack of a complete rotatio-
nal assigment of the transitions.

$S_1 ({}^1B_{2u})$ transition. The rotational spectrum was identical to
the one around 22 708 cm^{-1}. They were uniquely identified as
b-type perpendicular transitions, corresponding to a transit-
ion dipole moment parallel to the short molecular axis. The
non-totally symmetric b_{3g}-type vibration though has a very
different spectrum, which was identified as an a-type
(parallel) transition. All the spectral features were inde-
pendent of the type of seeding gas and therefore cannot be
due to VdW complexes of T with inert gas atoms. The $S_0 \rightarrow S_1$
electronic origin has a very strong spectrum (fig. 1) and
reduction of the laser power to as little as a few mW was
necessary to avoid strong saturation effects.

We assigned a total of 230 lines in the various spectra
(up to $J = 15$) and fitted them to an asymmetric rotor model
with an excellent fit. From the fit the rotational constants
were obtained in the ground and excited state, the identifi-
cation of the lines and the transition frequency ν_0. In
table 2 the rotational constants are listed for the ground

TABLE 2   Rotational constants of the tetracene molecule
           in the S_0 and S_1 electronic state ($\Delta A = A' - A''$,
           $\Delta B = B' - B''$, $\Delta C = C' - C''$).

S_0		S_1	
constant	(MHz)	constant	(MHz)
A	1630 (1)	ΔA	17.4 (1.2)
B	213.4(2)	ΔB	−1.81(8)
C	188.8(2)	ΔC	−1.19(8)

and excited electronic state. Within the experimental errors
no differences in the rotational constants of the various
vibrational states were observed.

The spectra of T are pure unperturbed rotational spectra
and we could assign all relevant spectral features. This in-
dicates that in the low vibrational energy range in the S_1
electronic state there is no clear intersystem crossing. The
interaction between the S_1 state and background states is
very weak although it is expected that a molecule as large as
T should be in the "statistical limit"[9]. The lifetimes of the
S_1 states (20 ns)[1] are such that the expected natural line-
width is still smaller than our experimental linewidth. This
is in accord with our observations.

3.1. Tetracene-argon VdW complexes

Tetracene-argon VdW complexes (T-Ar$_n$, n = 1,2,3, ...) are
easily formed in the molecular beam by using argon as seeding
gas. Operating our laser in the broadband mode (30 GHz band-
width) we observed vibrationally resolved spectra comparable
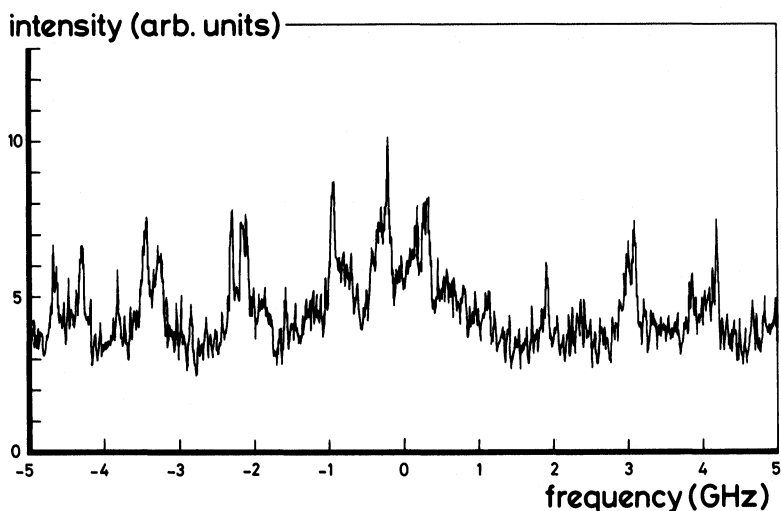with those of ref. 4 and ref. 5. The transitions in the com-

FIGURE 2 The $S_0 \rightarrow S_1$ electronic origin of the tetracene-argon Van der Waals complex at 22 354.86(5) cm^{-1}.

plexes are more or less regularly redshifted compared to the analogous transitions in T. Besides these shifts, the identification of the complexes is based on the pressure dependence of the intensity of the observed transitions.

Model calculations in the structure of the T-Ar complex[6] predict a favourable position of the Ar-atom above the molecular plane at a distance of about 3.45 Å and very near the middle of the T molecule. Although these calculations only give an indication of the structure of the complex we found similar calculations very satisfactory for the fluorene-argon VdW complex[2]. An experimental determination of the structure of this complex can be given by deriving the moments of inertia from the rotational spectra.

We recorded rotationally resolved spectra of transitions
in T-Ar analogous to the vibronic transitions in T mentioned
before (table 1). The spectrum around 22 354 cm^{-1} is assign-
ed as the electronic origin of the T-Ar complex (fig. 2).
It is of perpendicular type in common with the electronic
origin of T and it is almost identical to the transition at
22 666 cm^{-1}. The spectrum around 22 826 cm^{-1} belongs to a
different vibrational mode of T and is of parallel type. The
linewidth in these spectra is still determined by the resi-
dual Doppler width, in accordance with the expected natural
linewidth of 6 MHz[4]. We didn't succeed in assigning the pro-
nounced spectral features in the spectra of T-Ar. For in-
stance the sequence of Q-branches in the perpendicular spec-
tra looks distorted and there seems to be an excess of lines
in these spectra. We are convinced that there are perturba-
tions in the S_1 electronic state due to couplings with back-
ground states. This is in accord with the lifetime measure-
ments of ref. 4. The evidence for such coupling in these
complexes is more clear in the T-Kr complex where the per-
turbations are much larger.

3.3. Tetracene-krypton VdW complexes

By using krypton as seeding gas we produced $T-Kr_n$ (n =
1, 2, 3, ...) VdW complexes in the molecular beam. The tran-
sition frequencies (table 1) in the T-Kr complex have a
different shift from the corresponding transitions in T than
those of the T-Ar complex. This allows us to distinguish
between the various molecules and is very convenient to
check the identification of the transitions. The electronic
origin of the T-Kr complex around 22 330 cm^{-1} has a very
striking spectrum (fig. 3). Only rotational contours were
observed, due to the small rotational constants and a

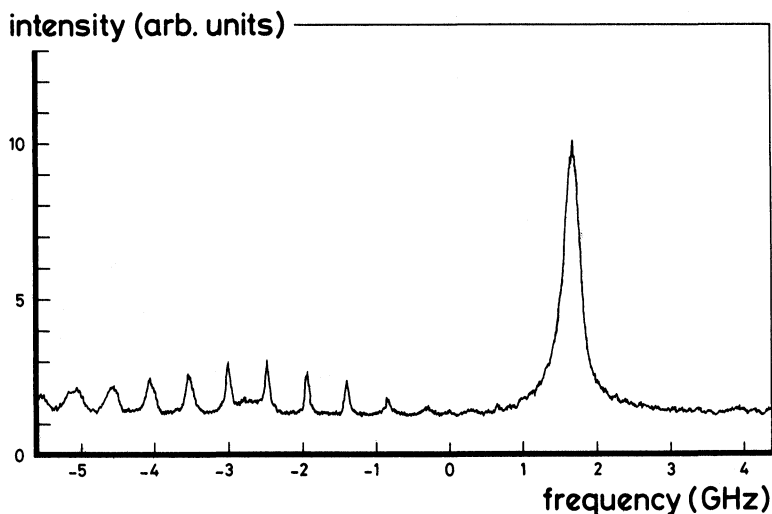FIGURE 3   The $S_0 \to S_1$ electronic origin of the tetracene-
            krypton Van der Waals complex at 22 329.6(7) cm^{-1}.

presumably increased linewidth[4]. The spectrum contains a
pronounced feature, resembling a Q-branch of a parallel
transition, and a sequence of weaker branches, characteristic
of a perpendicular transition. Besides this unusual contour
there is a rather strong background in the spectrum.

The vibronic transition of T-Kr connected to the a_g
vibrational mode of T mentioned before is very different
from the electronic origin of T-Kr. Note that this was not
the case in the T-Ar or the T molecule. This spectrum is
almost without any structure on a broad background.
It has been demonstrated[4] that the 311 cm^{-1} vibrational
excitations of T-Ar and T-Kr do not result in vibrational
predissociation on the time scale of the excited state life-

times. We conclude that the perturbed spectra are due to an intersystem crossing which is almost absent in T but is enhanced by addition of the inert gas atoms.

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