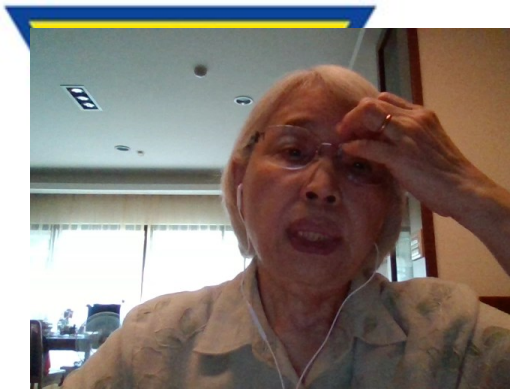
# The vibrational predissociation of the $\tilde{A}$ state of the $C_3Ar$ van der Waals complex with vibrational energy of 1558-1660 $cm^{-1}$


Sheng-Chang Hsiao and Yen-Chu Hsu

Department of Physics, National Central University, Taoyaun, Taiwan



MOST 科技部
Ministry of Science and Technology

# Introduction

- Extensive studies of the vibrational predissociation (VP) of the van der Waals (vdW) complex have been reported and most of them were studied in the time domain. It has been proposed that the VP rate is governed by the gap laws, the excited vibration mode, spectroscopic perturbation of the monomer, and $|\Delta v|$-propensity.
- The lifetime of the rare-gas atom complex can be as short as a few hundreds of pico-seconds or even shorter, its VP product state distribution is therefore a snap shot of the early stage of its IVR. Unfortunately, it is difficult to get the detailed product state distribution of a sizable complex with the available experimental methods. Only a few VP fragment state distributions have been reported. Thus, the knowledge of the VP processes and the IVR remains to be limited.
- In our previous work, we have shown that the $\tilde{A}^1\Pi_u$ state of the $C_3Ar$ van der Waals complex is a good system to study the VP processes because the spectroscopies of both $\tilde{A}$ and $\tilde{X}$ states of $C_3$ are well studied.
- The Renner effect ($\varepsilon$=0.537) of the $\tilde{A}$ state of $C_3$ makes this complex unique: a well-defined vibronic angular momentum P (=$\ell$+$\Lambda$) and the bending force constant of the upper R-T component is about 5 times of that of the lower component. Different from a degenerate $^1\Pi$ state, the Renner effect complicates the vibrational level structure, this system can be useful to study the effect of spectroscopic perturbation of the monomer to the VP processes of its complex.

$P = \ell + \Lambda$ , $\ell$ : the vibrational angular momentum of the $C_3$-L vibration and $\Lambda$ : the projection of the electronic orbital angular momentum degenerate electronic state.

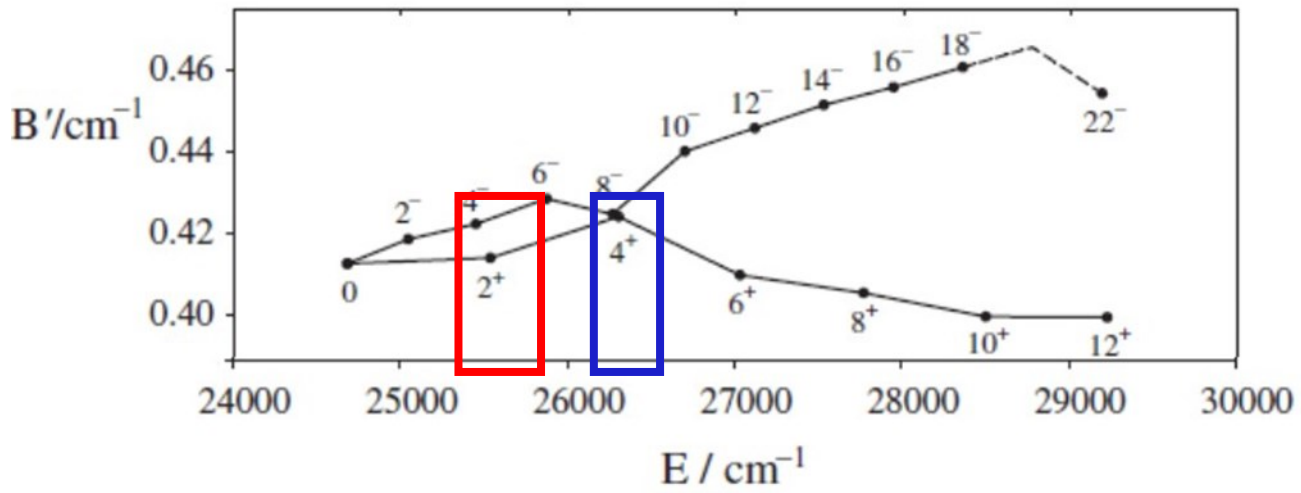
- An unusually low bending vibrational frequency of the $\tilde{X}$ state of $C_3$ is 63.4 $cm^{-1}$; its motion is expected to be of large amplitude.
- From the fragment branching ratios, it has been found that $|\Delta v|=1$ and $|\Delta P|=1$ propensities govern the VP processes in the low vibrational levels ~ 350-860 $cm^{-1}$ of the $\tilde{A}$ state. These propensities can be interpreted by a dipole-induced dipole interaction of the bending excited levels of $C_3$ and the Ar atom.
- Whenever the VP processes are near the dissociation threshold or vibrational mode-change is involved, the product branching ratio versus the excess energy $\Delta E$ (translational and rotational energies of a fragment), cannot be related by a gap law.
- Despite the fact that the upper levels were associated with the upper Renner component, 0 $2^+$ 0 level ($2^+$) of $C_3$, which interacts strongly with the $4^-$ level, the fragments were found in the lower Renner components only. In other words, the Renner effect (spectroscopic perturbation) did not affect the observed VP products.

Wang and Hsu, J. Chem. Phys. 2020.

# Motivation of this work:

As we just pointed out, no obvious Renner effect was found in the VP products of the complex levels associated with the $4^-/2^+$ Renner pair.

It will be interesting to go higher up to ~1560-1680 $cm^{-1}$ above the zero-point level of the Ã. Where the second Renner pair ($8^-/4^+$ pair) is expected. The interaction matrix element of the $8^-/4^+$ pair has been estimated to be about the same size (~20 $cm^{-1}$) as that of $4^-/2^+$ (~23 $cm^{-1}$) from the level structure of the Ã state of $C_3$. The energy gap of the $4^-/2^+$ pair is 87.4 $cm^{-1}$, that of the $8^-/4^+$ pair is down to 37 $cm^{-1}$. The Renner effect on the VP products of the $8^-/4^+$ pair will be studied.




C.-W. Chen et. al., J. Mol. Spectrosc. 2010.

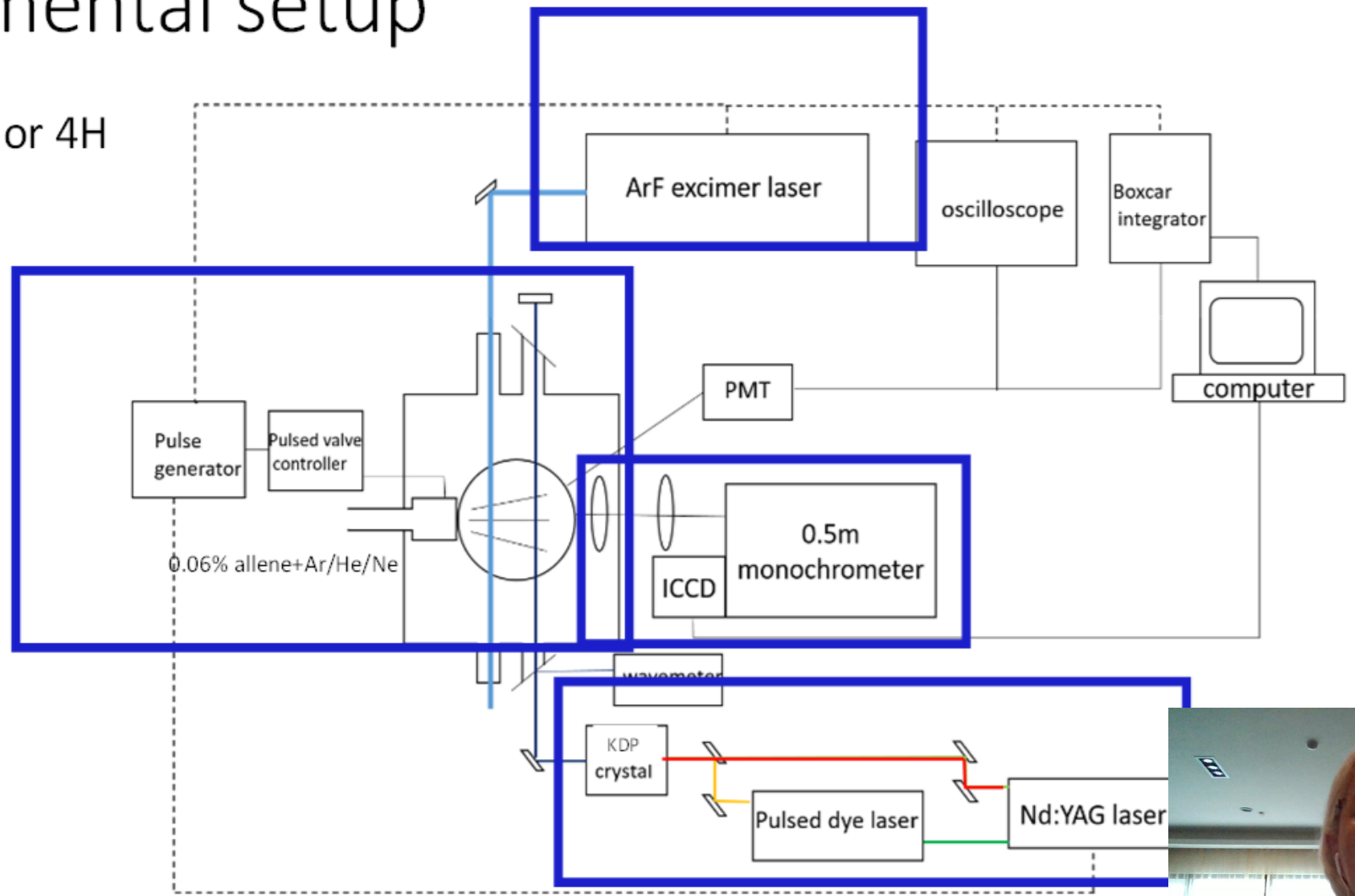
# Experimental setup

$C_3H_4 \xrightarrow{h\nu} C_3 + 2H_2$ or 4H

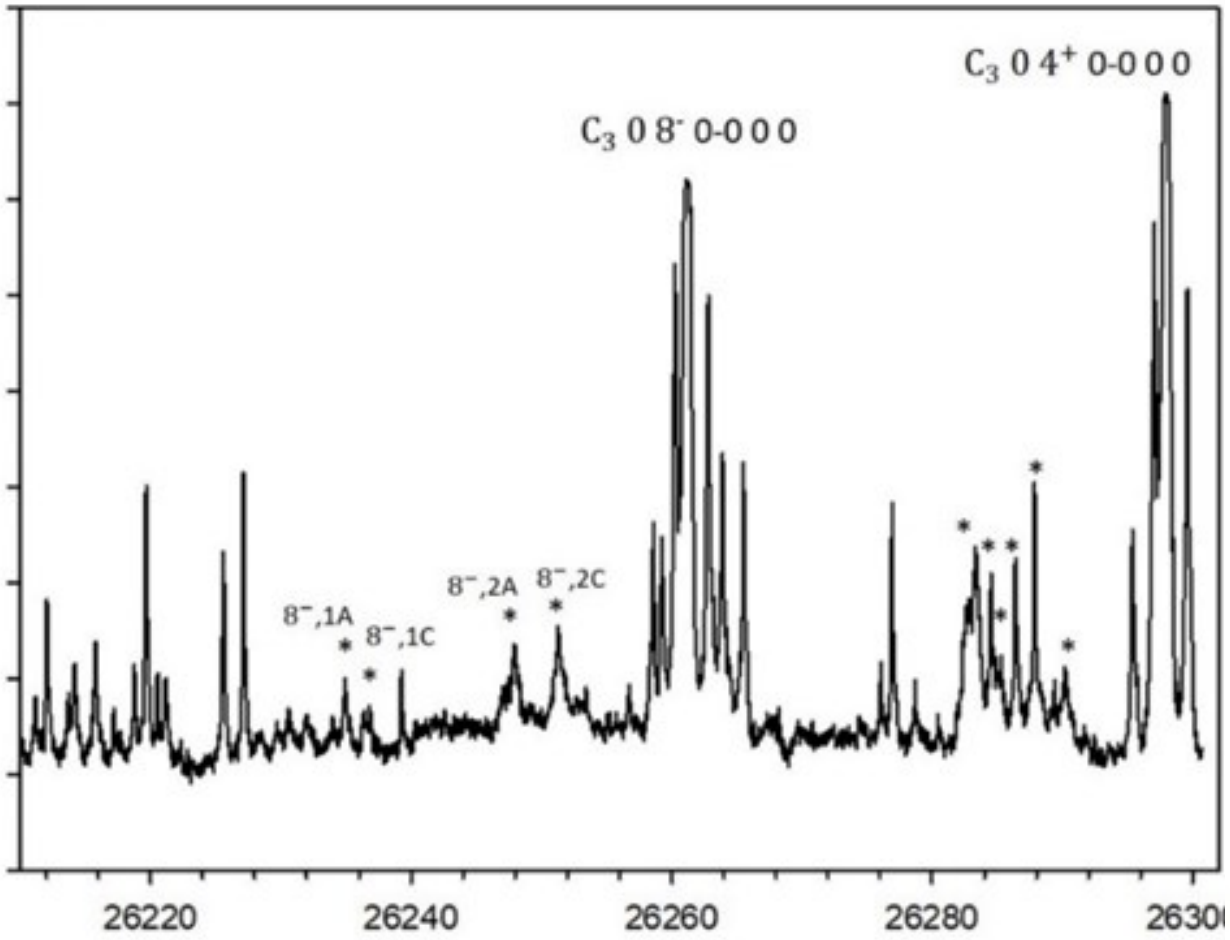
$C_3 + Ar \rightarrow C_3Ar$

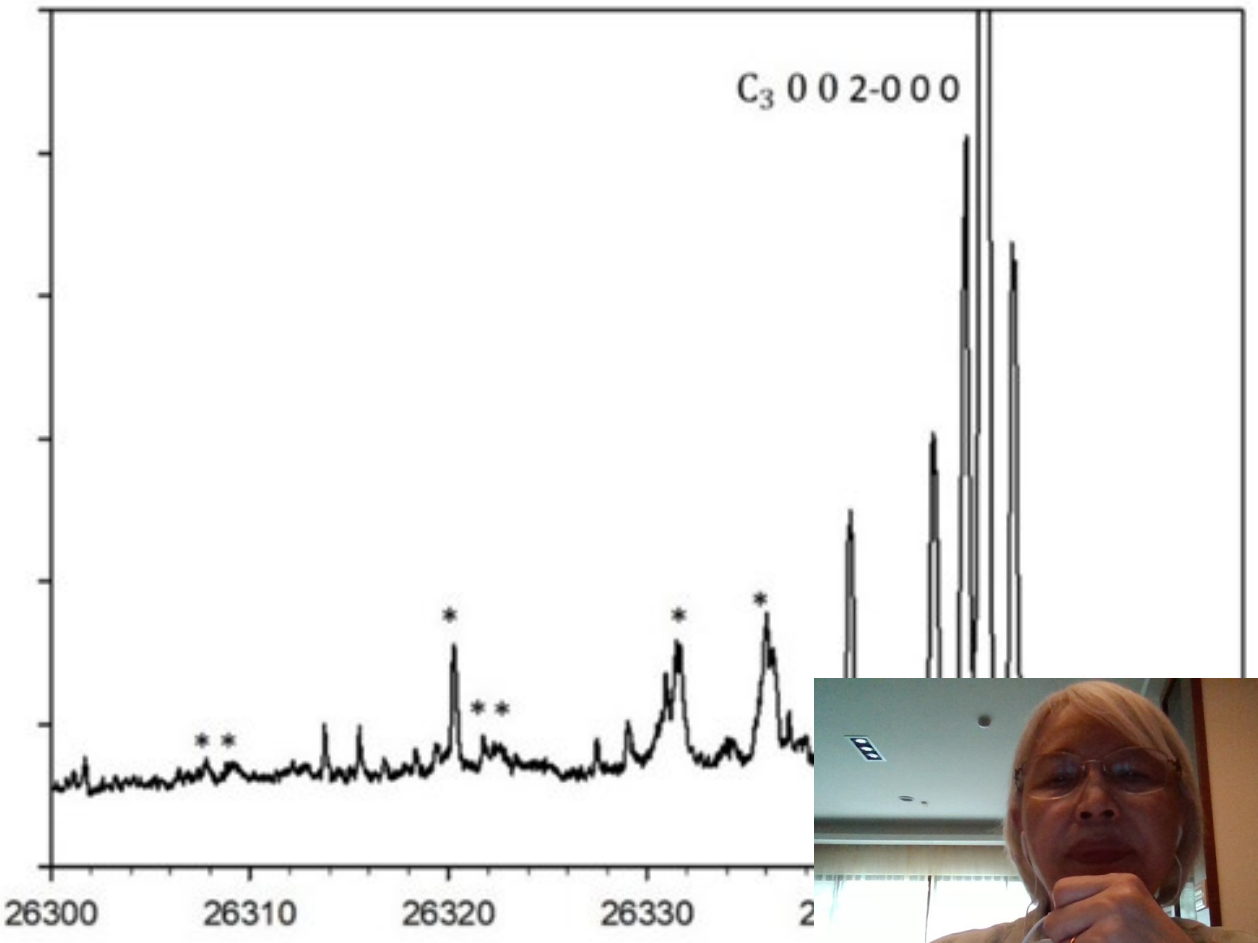
1. **Rotationally resolved LIF excitation spectrum**

2. **Wavelength-resolved emission spectrum**




# Excitation spectra of $C_3$ and $C_3Ar$ in the 26230-26360 $cm^{-1}$ region

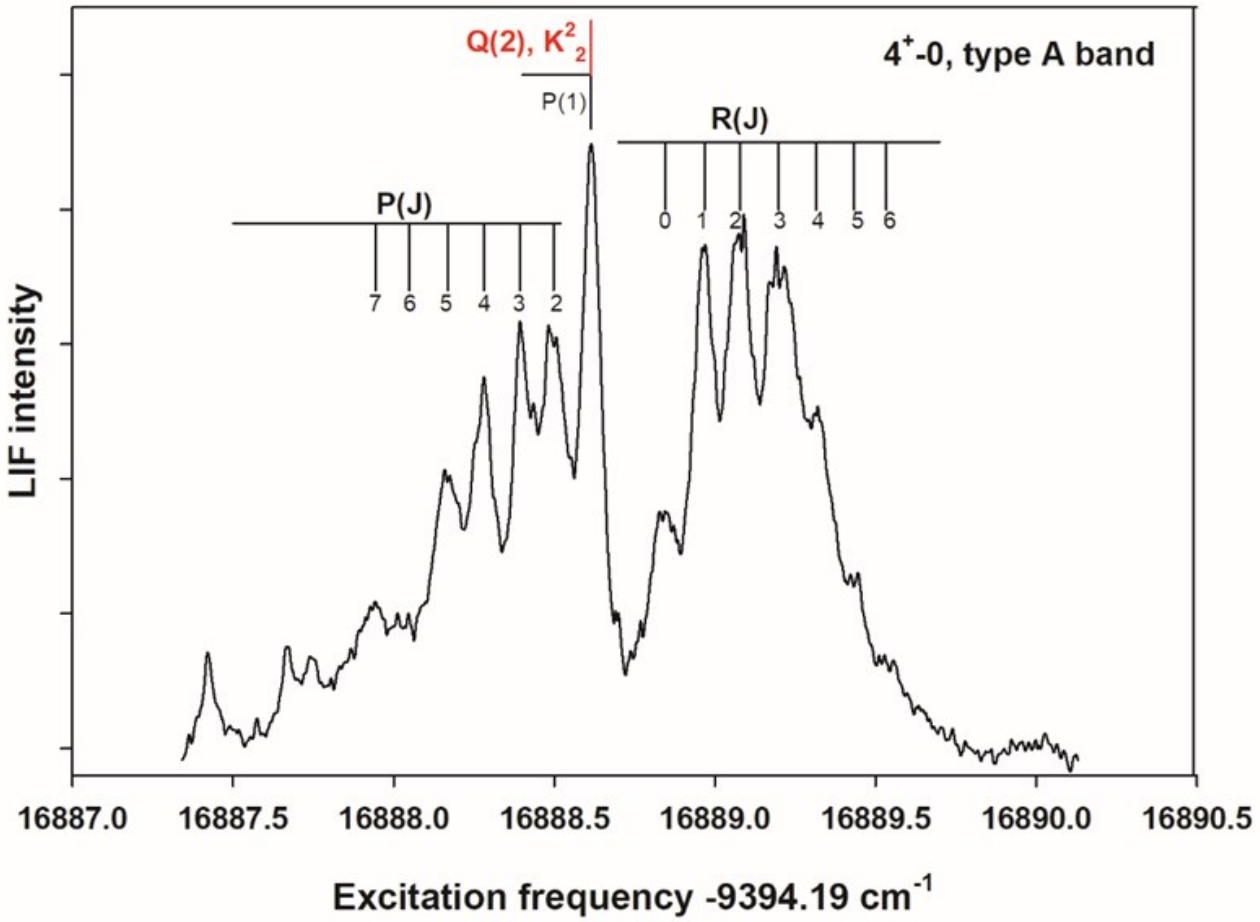


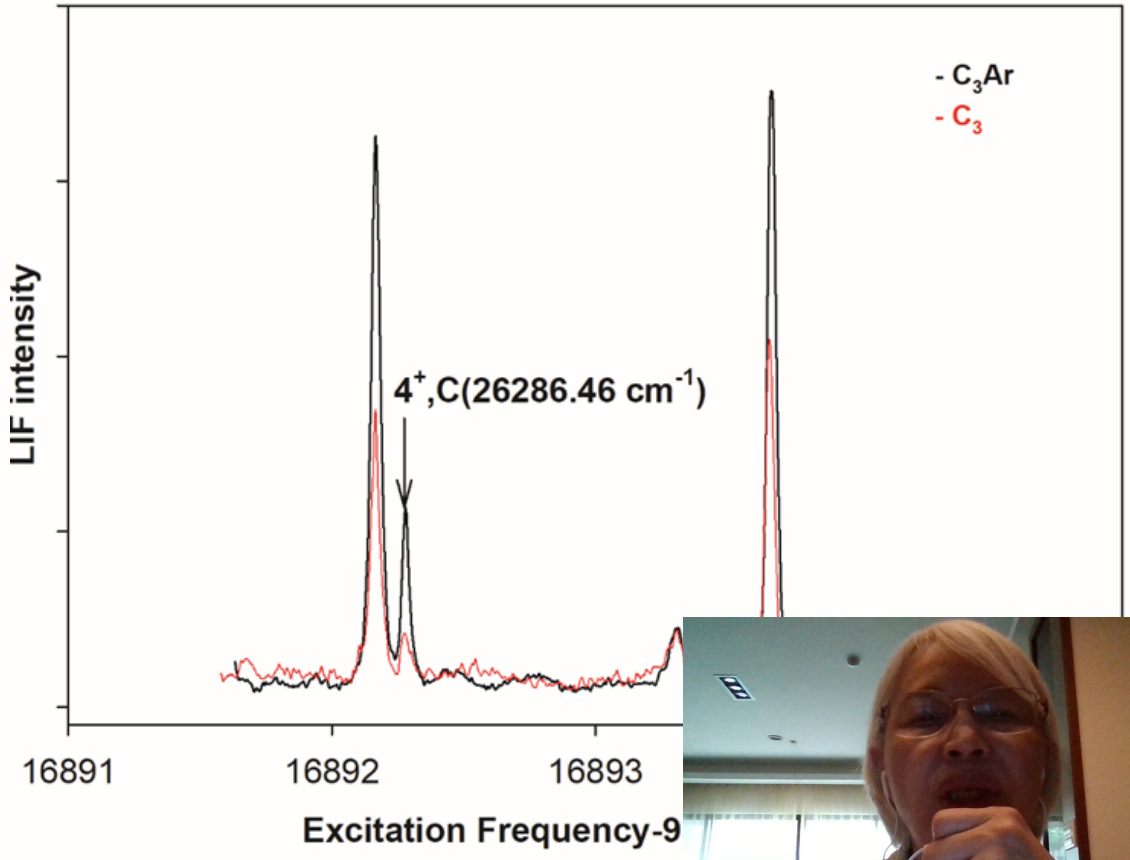



# The $C_3Ar$ bands studied in this work

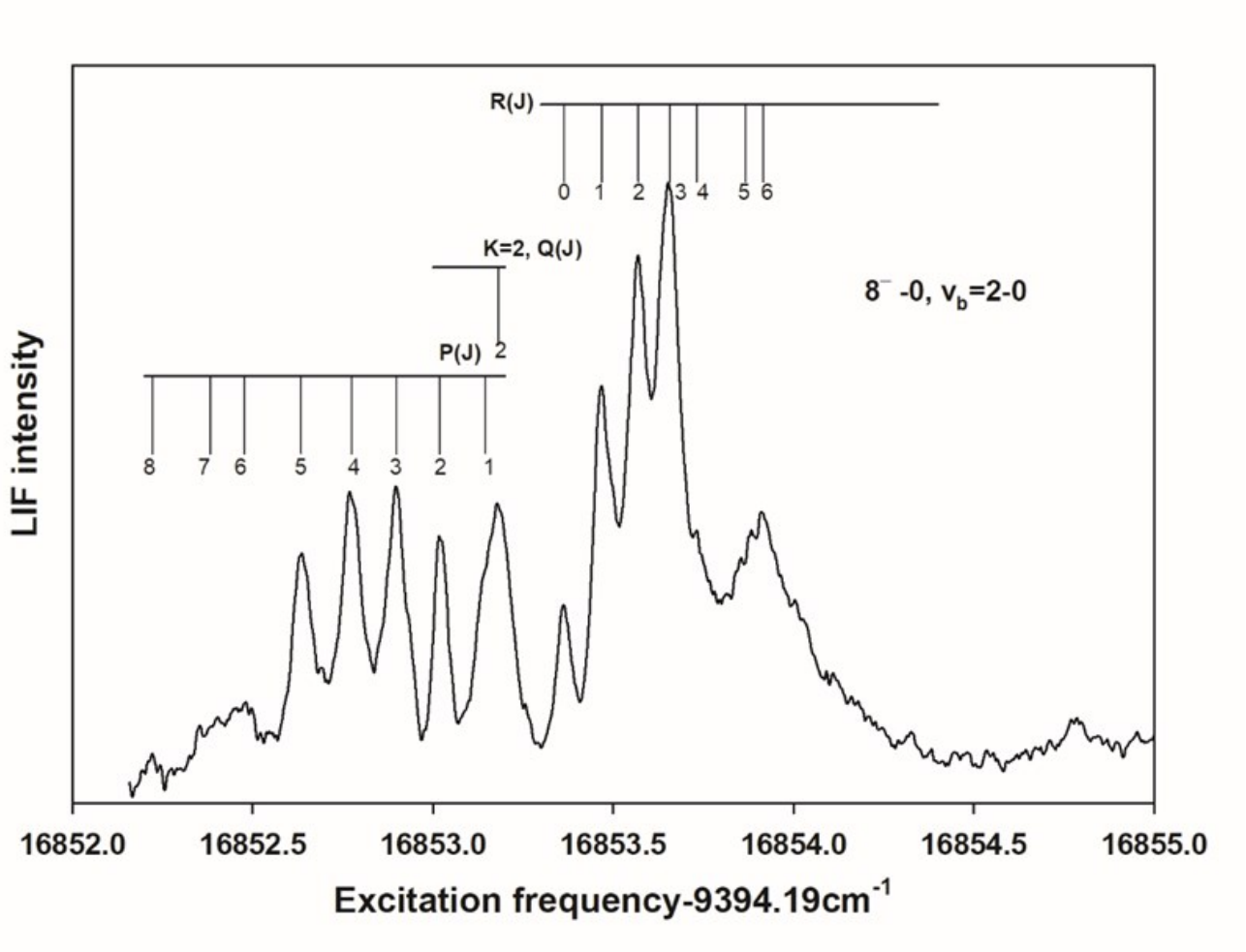
| | Band origin ($cm^{-1}$) | Vibrational assignment of the upper level of $C_3$ | Vibronic angular momentum of $C_3$, P | Spectral assignment of the vdW motion | Rotational angular momentum, K |
|---|---|---|---|---|---|
| $8^-$-0, 1A | 26234.9 | 0 $8^-$ 0 | 1 | $v_b$=0 | 0 and 2 |
| $8^-$-0, 1C | 26236.6 | 0 $8^-$ 0 | 1 | $v_b$=0 | 1 |
| $8^-$-0, 2A | 26247.8 | 0 $8^-$ 0 | 1 | $v_b$=2 | 0 and 2 |
| $8^-$-0, 2C | 26251 | 0 $8^-$ 0 | 1 | $v_b$=2 | 1 |
| $4^+$-0, 1A | 26283.3 | 0 $4^+$ 0 | 1 | $v_b$=0 | 0 and 2 |
| $v_3$=2-0, 1A | 26307.8 | 0 0 2 | 1 | $v_b$=0 | 0 and 2 |
| $v_3$=2-0, 1C | 26309.2 | 0 0 2 | 1 | $v_b$=0 | 1 |
| $v_3$=2-0, 2A | 26320.4 | 0 0 2 | 1 | $v_b$=2 | 0 ar |
| $v_3$=2-0, 2C | 26322.6 | 0 0 2 | 1 | $v_b$=2 | 1 |
| $v_3$=2-0, 3A | 26331.6 | 0 0 2 | 1 | $v_b$=4 | 0 |
| $v_3$=2-0, 3C | 26336 | 0 0 2 | 1 | $v_b$=4 | 1 |

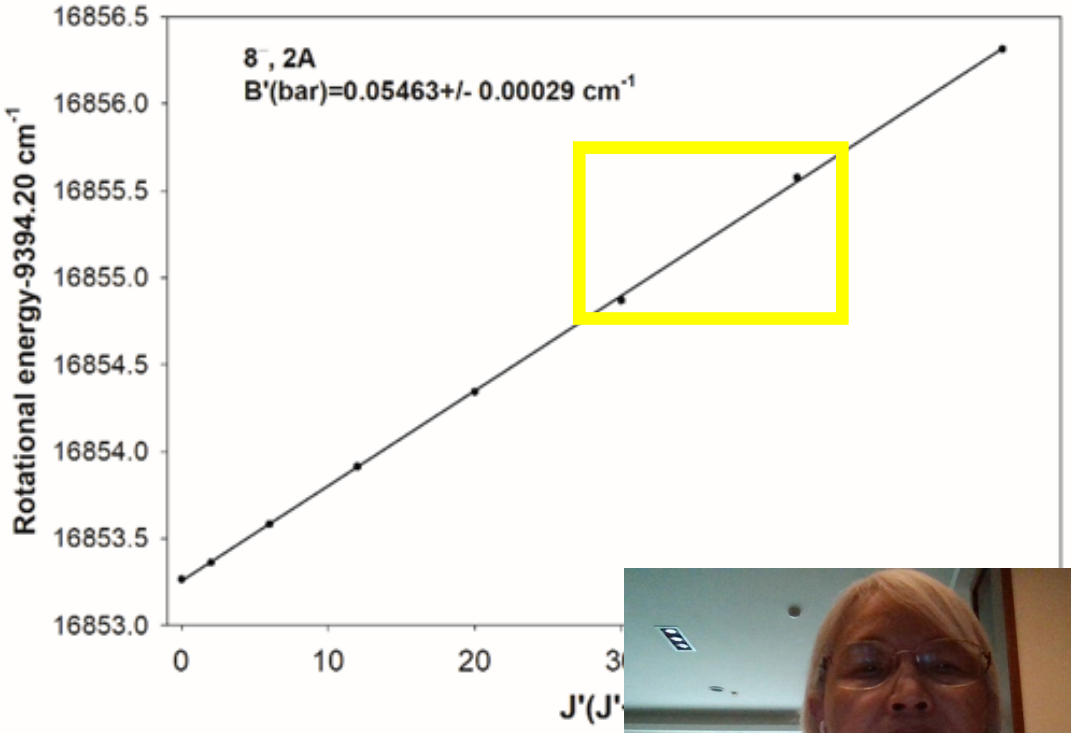
# $4^+$-0, $v_b$=0-0, type A and C bands



# $8^{-}$-0, $v_b$=2-0, type A band and perturbation




# Summary of the rotational analysis of the $C_3Ar$ bands

1. $\bar{B}'$

| | Type A band ($cm^{-1}$) | Type C band (cm-1) |
|---|---|---|
| $2^-$, $v_b'$=0 | 0.056672 | 0.05947 |
| $4^-$, $v_b'$=2 | 0.057045 | 0.06023 |
| $2^+$, $v_b'$=2 | 0.05681 | – |
| $8^-$, $v_b'$=2 | 0.05463±0.00029 | 0.06385±0.00034 |
| $4^+$, $v_b'$=0 | 0.05742±0.00011 | – |
| $v_3'$=2, $v_b'$=4 | 0.05762±0.00005 | 0.06116±0.00014 |

√

2. The perturbations of the $8^-$, $v_b'$=2 level were found at J'=5 and 6 near 26249.5 $cm^{-1}$. The perturbing state was tentatively assigned as the complex levels associated with $C_3$, $\tilde{A}$, $1\,1^+\,0$, $\Sigma_g$. It leads to a sl longer vdW bond length. We do not know why the $\bar{B}'$ of the ty deviates from the rest with a slightly shorter vdW bond length.

# Vibrational levels of $C_3(\tilde{A})$ in the energy of 26092-26339 $cm^{-1}$

$1\,3^-\,0, \Sigma_g$

26319.1

$1\,2^-\,0, \Phi_u$ 26267.8

$1\,1^+\,0, \Sigma_g$ 26243 √

26127.3

$1\,2^-\,0, \Pi_u$

$0\,8^-\,0, \Phi_u$

26339.0

$0\,4^+\,0, \Pi_u$ 26297.1

$0\,8^-\,0, \Pi_u$ 26260.3 √

$0\,4^+\,0, \Phi_u$ 26211.6

$0\,7^-\,0, \Gamma_g$ 26157.0

$0\,7^-\,0, \Delta_g$ 26092.2

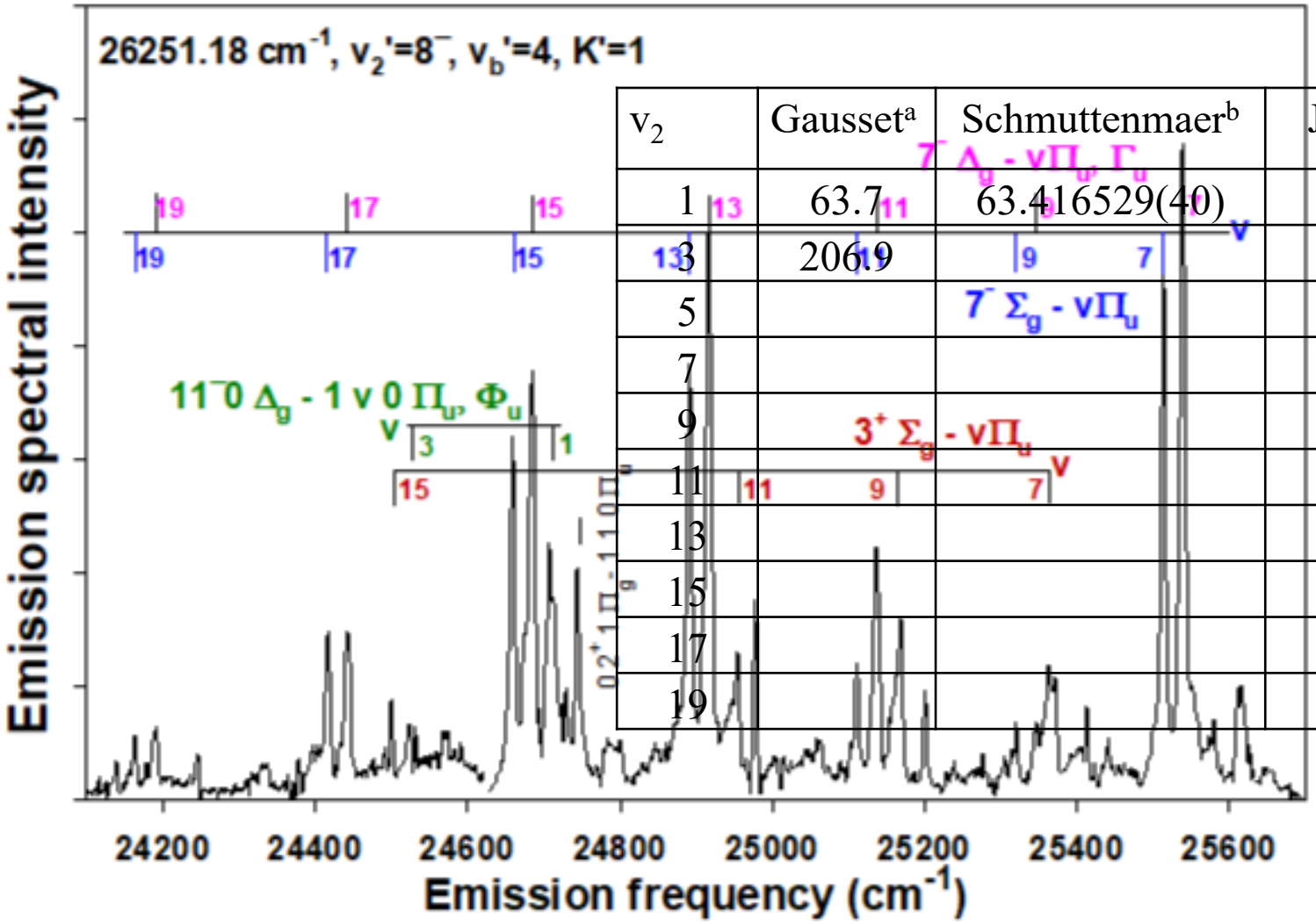
# Summary of the rotational analysis of the $C_3Ar$ bands

3. The $C_3Ar$ spectral features near 26288-26290 $cm^{-1}$, having different band contours from others, were attributed to hot bands. A weak feature at 26286.46 $cm^{-1}$ was likely to be the Q line of the type C band. But, it is difficult to have a rotational analysis.

4. Extra lines have been found in the type A band of the $3^2_0$, $v_b{}^4{}_0$ transition. These extra lines belong to a $K^0_0$ band and are above the $3^2$, $v_b{}^4$ by 0.35 $cm^{-1}$. This interaction could be of Fermi resonance, but the perturbing state has not been identified.

5. In this higher energy region, perturbations were found more than the lower energy region, which is expected.

# New spectroscopy obtained from the emission spectra of $C_3Ar$




| $v_2$ | Gausset[a] | Schmuttenmaer[b] | Jungen[c] | Mladenović[d] | This work |
|---|---|---|---|---|---|
| 1 | 63.7 | 63.416529(40) | 63.10 | 64.301 | 63 |
| 3 | 206.9 | | 207.22 | 206.515 | 207 |
| 5 | | | 370.21 | 365.030 | 372 |
| 7 | | | 548.62 | 539.737 | 553 |
| 9 | | | | 729.508 | 745 |
| 11 | | | | | 955 |
| 13 | | | | | 1175 |
| 15 | | | | | 1407 |
| 17 | | | | | |
| 19 | | | | | |