VISIBLE PHOTODISSOCIATION SPECTRA OF THE
1-METHYL AND 2-METHYLNAPHTHALENE CATIONS:
LASER SPECTROSCOPY AND THEORETICAL SIMULATIONS

H. FRIHA, G. FERAUD, C. FALVO, P. PARNEIX, T. PINO, Ph. BRECHIGNAC,
Institut des Sciences Moléculaires d’Orsay, Université Paris-Sud, Orsay, France;

TYLER TROY, TIMOTHY SCHMIDT, School of Chemistry, The University of
Sydney, Sydney, NSW, Australia;

ZOUBEIDA DHAOUADI, LSAMA, University Tunis El Manar, Tunis, Tunisia.

PAH cations in space and the DIB’s spectra
Methyl substitution is relevant for astro-PAHs
Tan, X.; Majewski, W.; Plusquellic, D.; Pratt, D.  
*Methyl-group torsional dynamics from rotationally resolved electronic spectra: 1-methylnaphthalene and 2-methylnaphthalene.* NEUTRALS  
The experimental challenge of PAH cations

Shida & Iwata, 1973

Low temperature Freon matrix

Total spectral shift: 915 cm$^{-1}$
Similar results in argon matrix

Andrews, L.; Kelsall, B.; Blankenship, T.

*Vibronic absorption spectra of naphthalene and substituted naphthalene cations in solid argon.*


What about the gas-phase spectrum?
The « Argon tagging trick »

In the case of aromatic species, the electronic spectrum of the bare cation can be deduced by such tagging photodissociation spectroscopy when the properties of the aromatic chromophore \( M \) solvated by RG atoms are known in the \( M^+-(RG)_n \), \( n=1,2 \) clusters.

The observed perturbation, due to the solvation, is known as the **electronic shift** and is additive upon an increasing number of rare gas atoms.

Nowadays widely spread …
Experimental set-up

Preparation just above IP: Cold cations

Molecular beam
TOF

R2C2PI

Cold cations
Principle of the technique

- Principle of the technique
- T.O.F.MS
- MCP-Detector
- Other Fragments
- $^1\text{C}_{10}\text{H}_8^+$
- $^1\text{C}_{10}\text{H}_8^+$
- Delayed $^1\text{C}_{10}\text{H}_8^+$
- $^1\text{C}_{10}\text{H}_8^+$-Ar
- Ion current (a.u.)
- $h\nu_1$
- $h\nu_2$
- $h\nu_3$
- $D_0$
- $S_0$
- $S_1$
- $D_n$
How to record a spectrum of PAH\textsuperscript{+}-argon?

From the ion signals

Spectrum = Fragmentation ratio versus laser wavelength
A change of protocol

Ions, formed right at the exit of the nozzle, freely fly until they are extracted by a delayed voltage pulse.

A typical TOF

Multiplex recording
The photodissociation spectra

An Optical Parametric Oscillator (0.2 cm$^{-1}$ bandwidth; Spectra-Physics) was used to photodissociate the cations in the 680–580 nm range.

- **1-Me-Np$^+$**
  - FWHM $\approx 130$ cm$^{-1}$
- **2-Me-Np$^+$**
  - Intrinsic FWHM 20-25 cm$^{-1}$
- **Np$^+$**

**N$_2$ tagging**

**Ar tagging**
The Van der Waals spectral shifts: recovering the free gas-phase values

Simple extrapolation

Shift from the origin (cm⁻¹)

Number of N₂ or Ar

1-Me-Np⁺_(N₂)ₙ
2-Me-Np⁺_(N₂)ₙ
2-Me-Np⁺_Arₙ
The main results

The 1-methylnaphthalene$^+$: red shift of 808 cm$^{-1}$, relative to the band of naphthalene$^+$.

$D_2$—$D_0$ at 14 906 cm$^{-1}$

2-methylnaphthalene$^+$: blue shift of 226 cm$^{-1}$.
Separation of the hindered rotor motion from the other intramolecular modes

\[ H_\alpha(\theta, q) = H_\alpha^{\text{rot}}(\theta) + H_\alpha^{\text{vib}}(q) \quad \text{full decoupling of} \ \theta \]

Harmonic and Born–Oppenheimer approximations using the cumulant Gaussian fluctuations formalism (CGF)

(Franck-Condon-like)


DFT calculations B97-1 functional, 6-31G* basis set
Hindered rotation

\[ H_\alpha^{\text{rot}}(\theta) = -B_\alpha \frac{\partial^2}{\partial \theta^2} + V_\alpha(\theta) \]

\[ V_\alpha(\theta) = \frac{1}{2} V_{\alpha,3}(1 - \cos(3\theta)) + \frac{1}{2} V_{\alpha,6}(1 - \cos(6\theta)) \]

Fit of the Electronic Structure Data

<table>
<thead>
<tr>
<th></th>
<th>( B_\alpha ) (cm(^{-1}))</th>
<th>( V_{\alpha,3} ) (cm(^{-1}))</th>
<th>( V_{\alpha,6} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Me–Np+ (D(_0))</td>
<td>5.33</td>
<td>439.4</td>
<td>-31.5</td>
</tr>
<tr>
<td>1Me–Np+ (D(_2))</td>
<td>5.30</td>
<td>1226.1</td>
<td>-64.1</td>
</tr>
<tr>
<td>2Me–Np+ (D(_0))</td>
<td>5.31</td>
<td>81.3</td>
<td>-0.6</td>
</tr>
<tr>
<td>2Me–Np+ (D(_2))</td>
<td>5.32</td>
<td>-92.7</td>
<td>-2.1</td>
</tr>
</tbody>
</table>

For comparison: Methylanthracene \( S_0 \quad V_6 \sim 100 \text{ cm}^{-1} \) or less (Baba, 2009)
Extension of the Cumulant Gaussian Fluctuations formalism to include the internal rotation.

Strong hindering

Weak hindering

Rich internal rotation structure
Comparison of experiment and theory

Internal rotation at $T=30$ K

VdW modes not taken into account

Lorentzian convolution $\delta=20$ cm$^{-1}$

Intrinsic broadening due to internal conversion rate

*Excellent agreement!*

Not a temperature effect
Thank you very much for your attention

Full reference for this work:
dx.doi.org/10.1021/jp407627x  J. Phys. Chem. A 2013, 117, 13664