Large Amplitude Motion Effects in the TPE Spectrum of Methyl Isocyanate

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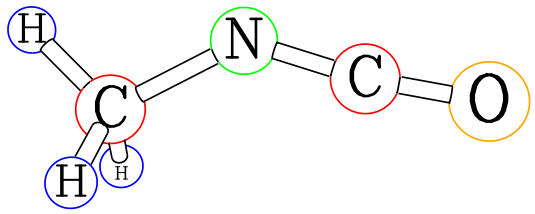
[c]DESIRS beamline, Synchrotron SOLEIL, Gif-sur-Yvette, France
[d]ENSC, Univ. Rennes, Rennes, France

ISMS, June 17–21, 2019

Outline



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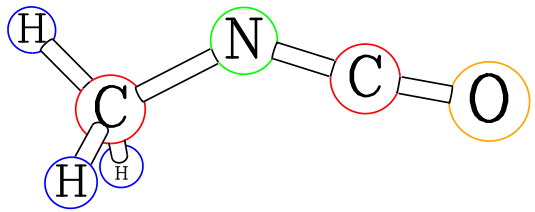

- Microwave & photoelectron spectra

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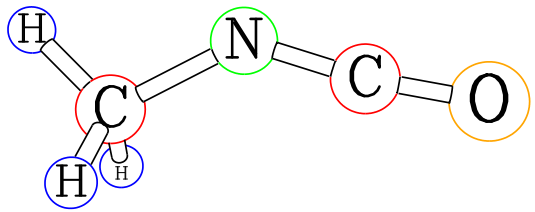

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- Threshold photoelectron spectrum (TPES) recorded in this work

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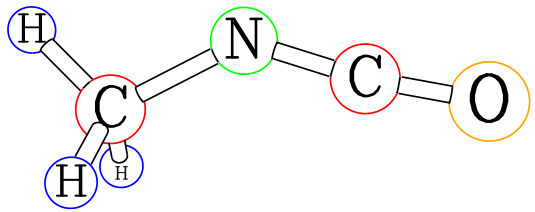

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- Threshold photoelectron spectrum (TPES) recorded in this work
- How should this spectrum be modeled

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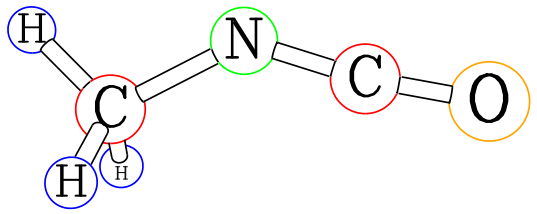
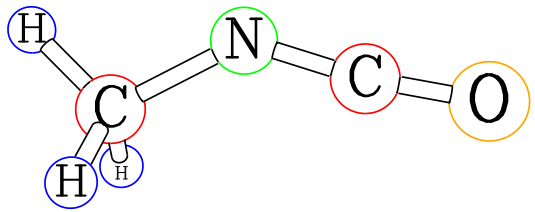


- Microwave & photoelectron spectra
- Threshold photoelectron spectrum (TPES) recorded in this work
- How should this spectrum be modeled
- Comparisons between observed and calculated TPES

The microwave spectrum



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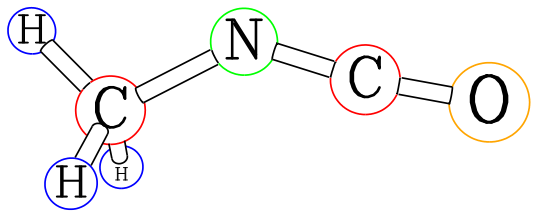
The microwave spectrum



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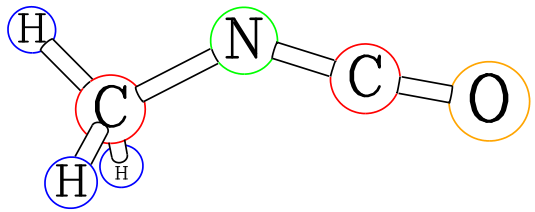

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- Two large amplitude motions need to be accounted for to reproduce the frequency of *a*-type lines[2]

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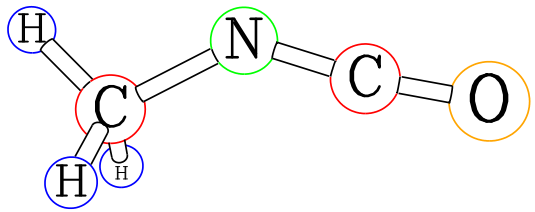

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- Detected in the Orion clouds[3]

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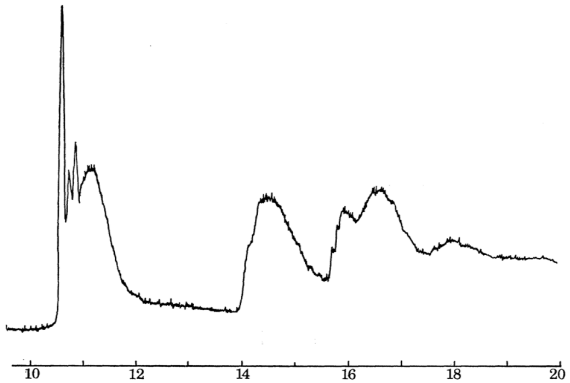
The photoelectron spectrum



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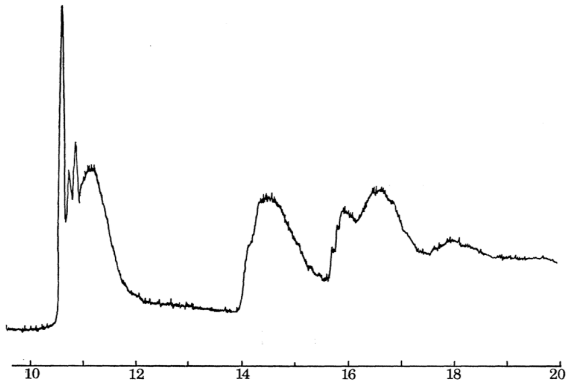

- The photoelectron spectrum has been investigated and spectra spanning the energy range from 10 to 18 eV were recorded[1–3]

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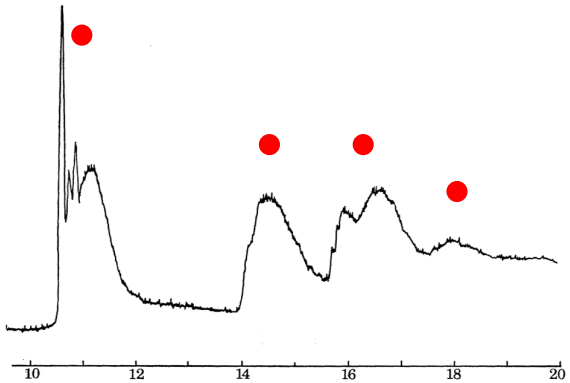

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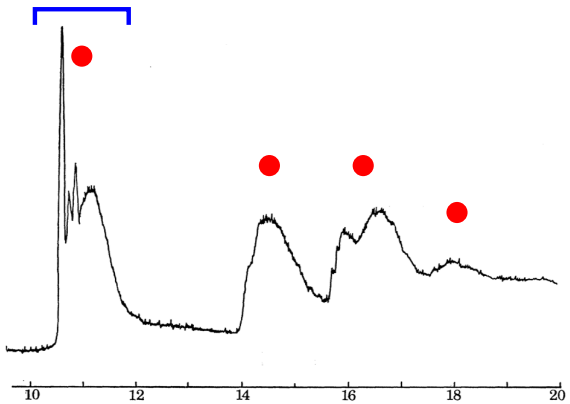

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- In this talk, the low energy band, from 10.4 to 12 eV, is investigated with a higher resolution

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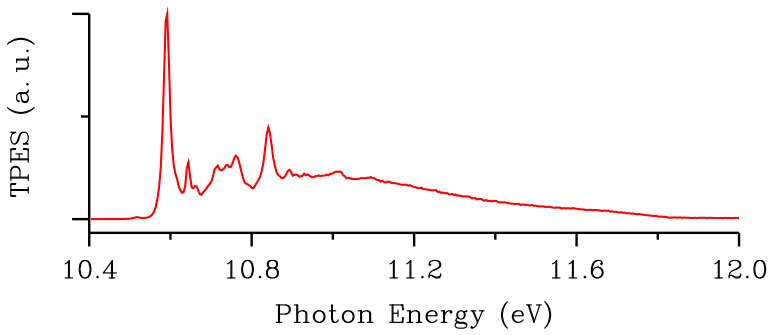
The TPES recorded in this work



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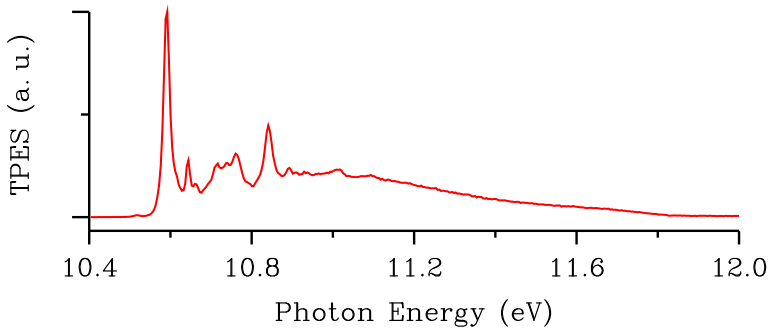

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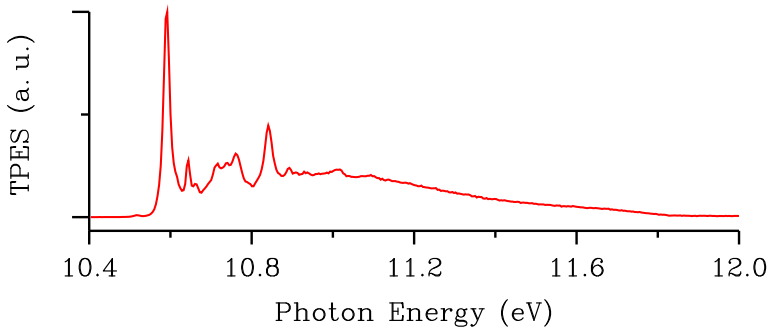
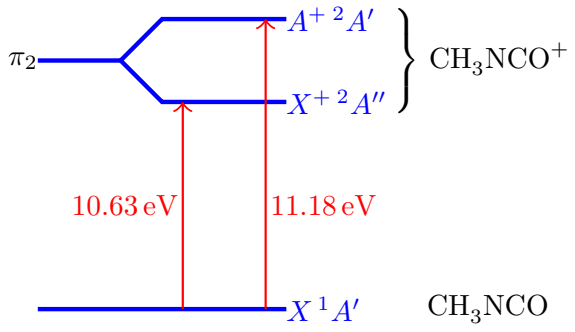


- A TPES was recorded using synchrotron radiation
- Energy difference between cation & neutral levels

$$h\nu = E(\mathrm{CH_3NCO^+}) - E(\mathrm{CH_3NCO})$$

Spectrum modeling



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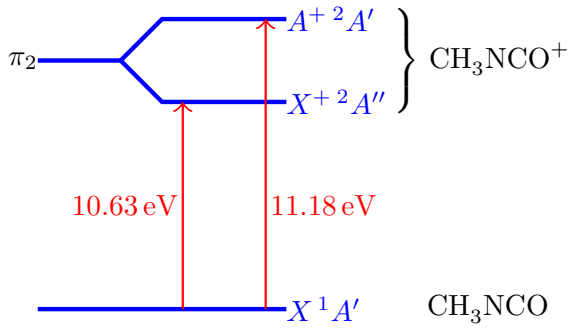

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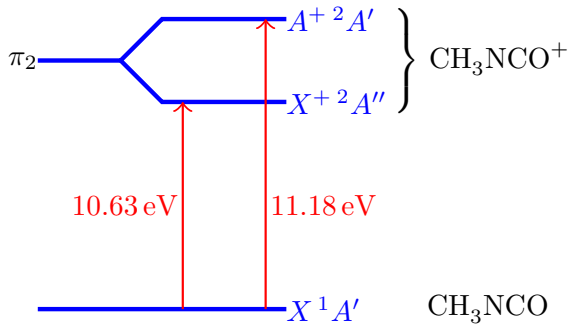

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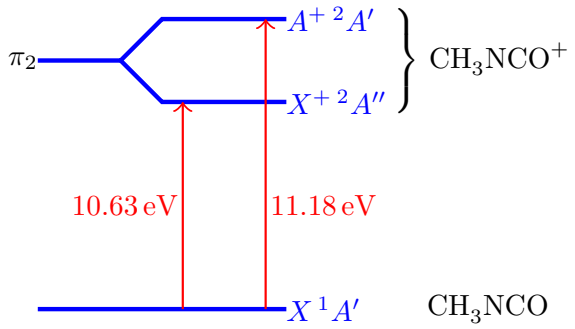

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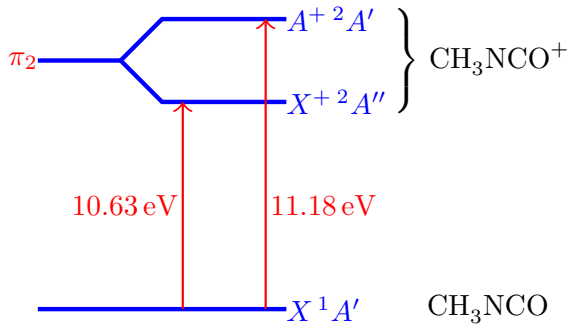

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- The π_2 orbital is located at the NCO group[1,2]

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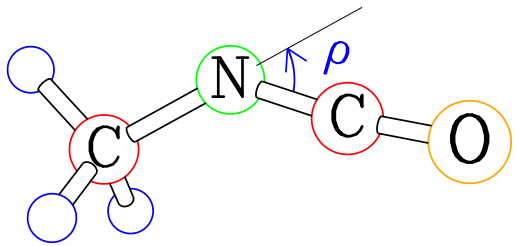

Bending mode

$t = \cos(\pi - \rho)$

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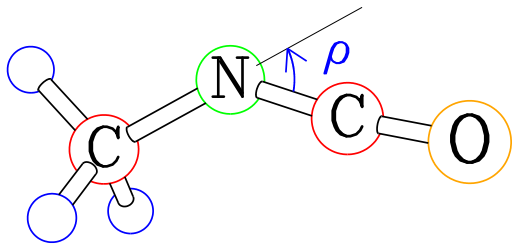

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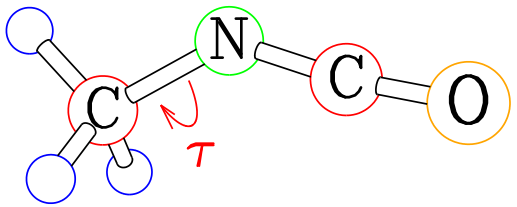
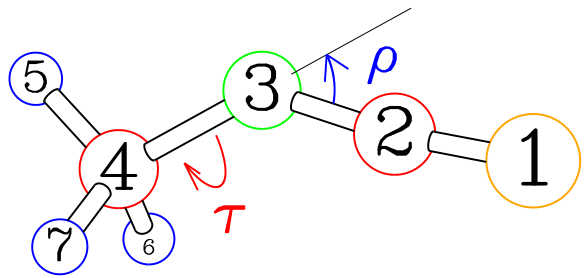


Torsion

τ

Energy level calculation: Kinetic energy

A reference configuration $\mathbf{a}(\rho, \tau)_i$, with $1 \leq i \leq 7$, is chosen



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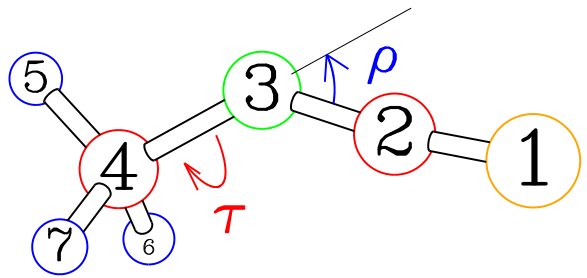

Bending-Torsion-Rotation energy levels are calculated with a 5-dimensional Hamiltonian[1,2]

$$H(t, \tau, \Omega)$$

using the 5×5 generalized inverse inertia tensor $\boldsymbol{\mu}(t, \tau)$

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Energy level calculation: Potential energy surface

The bidimensional potential energy surface is written

$$V(\rho, \tau) = V_0(\rho) + \frac{1}{2}\rho V_3^1 \cos 3\tau$$

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[2] Dalbouha, Senent *et al.*, *J. Chem. Phys.* **145** (2016) 124309
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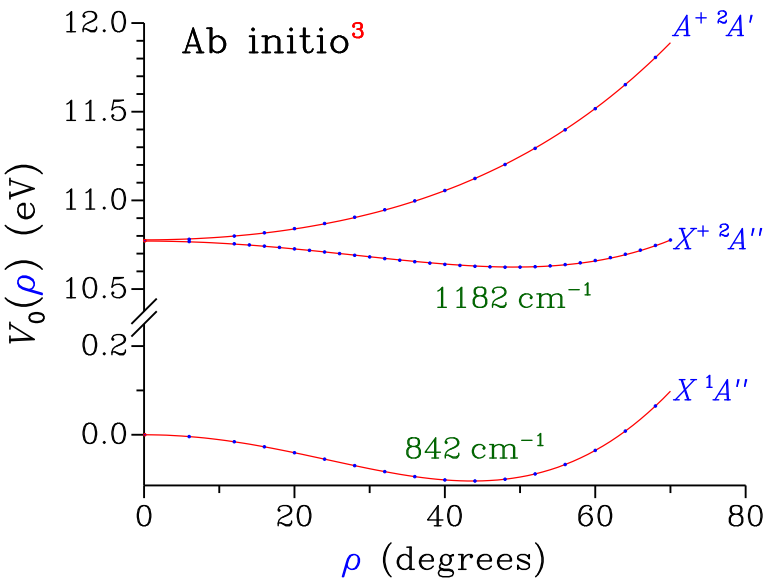

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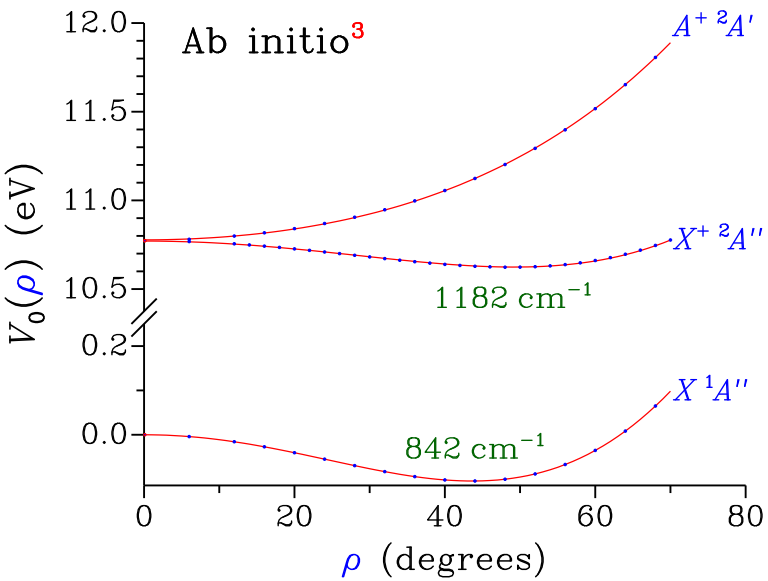

State	V_3^1/cm^{-1}
$X\,^1A'$	20,[1] 16.2,[2] 44.5[3]
$X^+\,^2A''$	235.5[3]
$A^+\,^2A'$	?

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Energy level calculation: Basis set functions

Bending-torsion-rotation basis set functions

$$(1-t)^{\alpha/2}(1+t)^{\beta/2}P_n^{(\alpha,\beta)}(t) \quad \exp(im\tau)/\sqrt{2\pi} \quad |J,k,M\rangle$$

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Singularity at the linear $t=-1$ configuration

$$\mu(t)_{zz},\ \mu(t)_{\tau z},\ \text{and}\ \mu(t)_{\tau\tau} \simeq \frac{1}{1-t^2}$$

accounted for taking appropriate values[1] for α and β

[1] Coudert, *J. Molec. Spectrosc.* **104** (1989) 123

Energy level calculation: Results

Calculated $J = 1$ bending-torsion-rotation energies for the neutral

A_1					A_2					E				
v_b	k	m	Cal[1]	Cal[2]	v_b	k	m	Cal[1]	Cal[2]	v_b	k	m	Cal[1]	Cal[2]
0	1	0	4.15	4.15	0	0	0	0.00	0.00	0	−1	1	5.13	5.13
0	−1	3	61.17	61.17	0	1	0	4.15	4.15	0	0	1	8.71	8.70
0	0	3	80.17	80.17	0	−1	3	61.17	61.17	0	1	1	18.95	18.95
0	1	3	107.16	107.16	0	0	3	80.46	80.46	0	−1	2	26.51	26.51
1	1	0	196.22	196.18	0	1	3	107.16	107.16	0	0	2	36.33	36.33
					1	0	0	191.34	191.30	0	1	2	55.75	55.75
					1	1	0	196.22	196.18	0	−1	4	115.34	115.29
										0	0	4	141.77	141.73
										0	1	4	175.46	175.41
										0	−1	5	186.71	186.67
										1	−1	1	196.49	196.45
										1	0	1	200.81	200.77

[1] Koput, *J. Molec. Spectrosc.* **106** (1984) 12
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The $X^+\,^2A'' \leftarrow X\,^1A'$ ionizing transition @ 10K

Selection rules for rotational components $\begin{cases} |\Delta J| \leq 2,\ |\Delta k| = 1 \\ A_{1,2} \leftrightarrow A_{1,2} \quad \text{or} \quad E \leftrightarrow E \end{cases}$

[1] Willitsch & Merkt, *Int. J. Mass Spectrosc.* **245** (2005) 14

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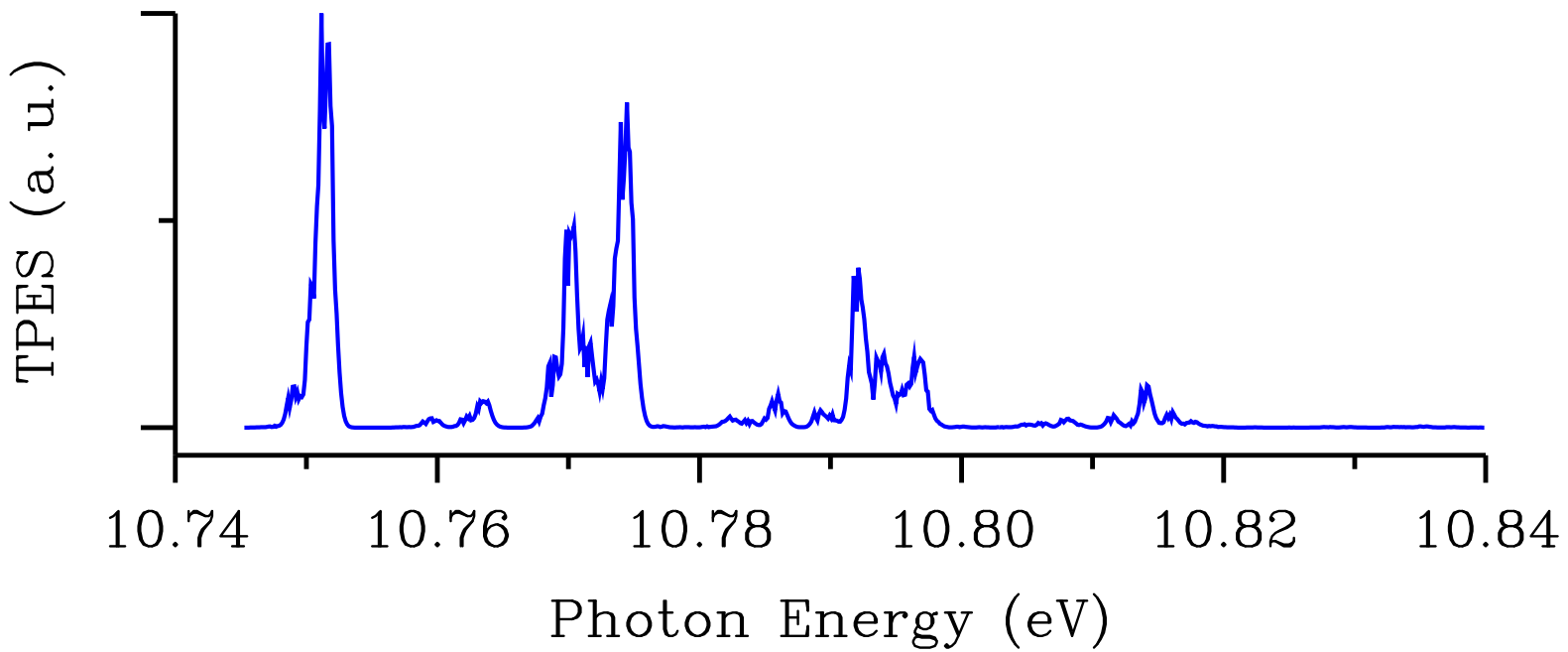

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The $X^+\,^2A'' \leftarrow X\,^1A'$ ionizing transition @ 10K

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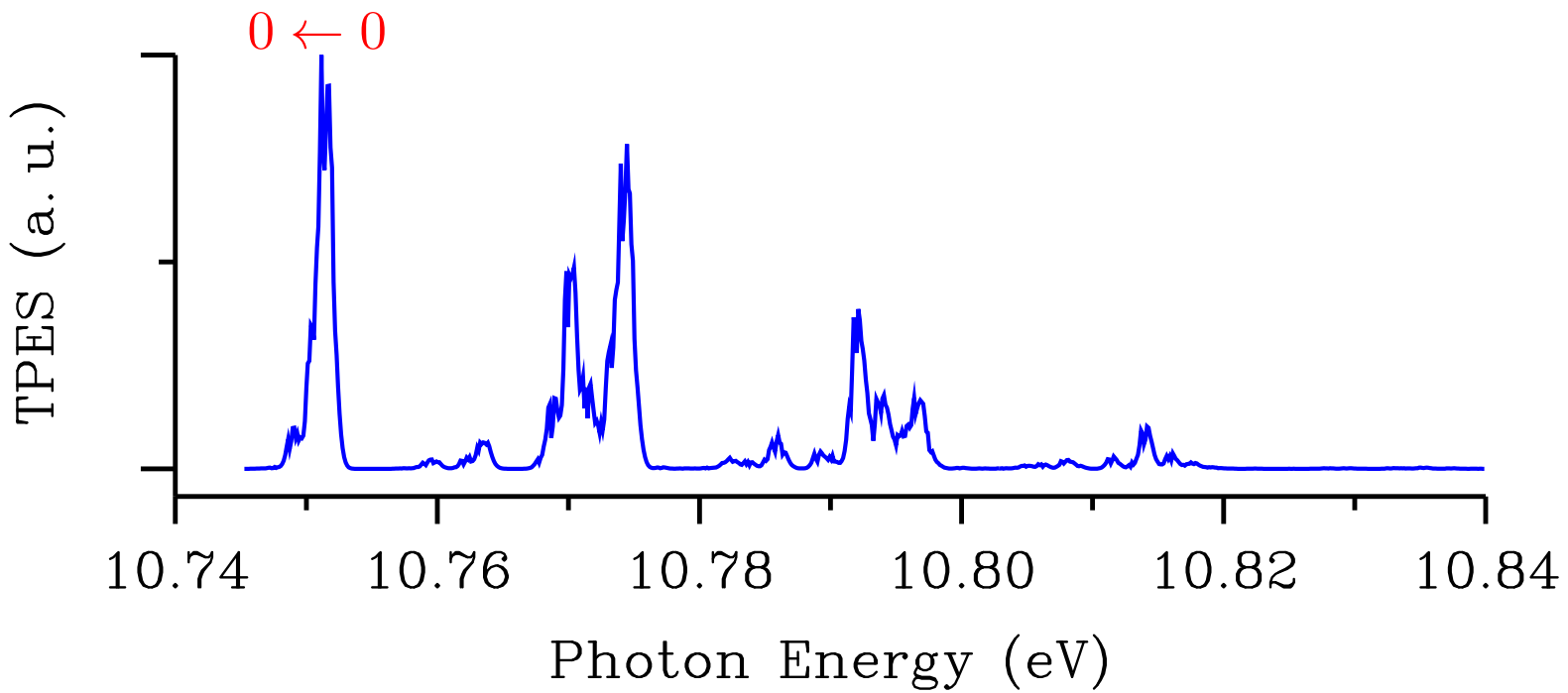

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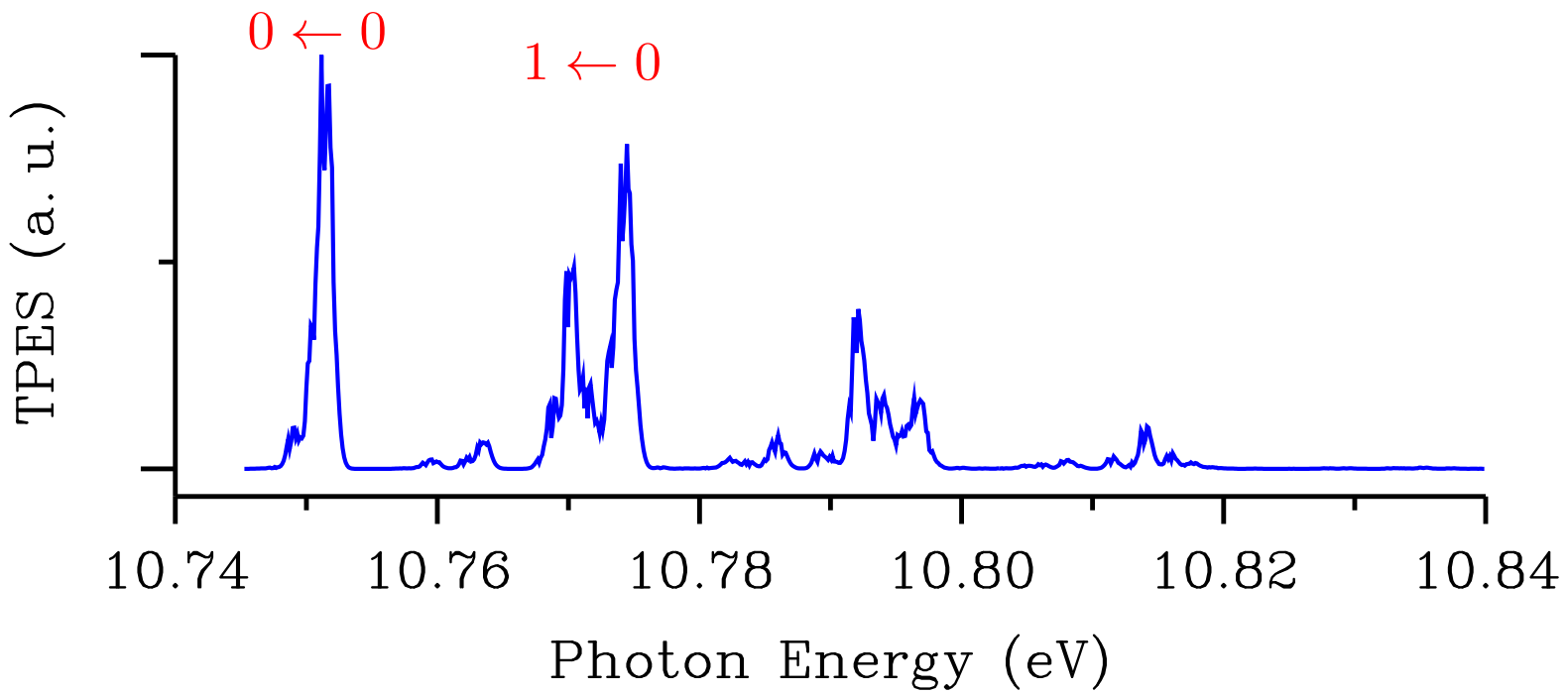

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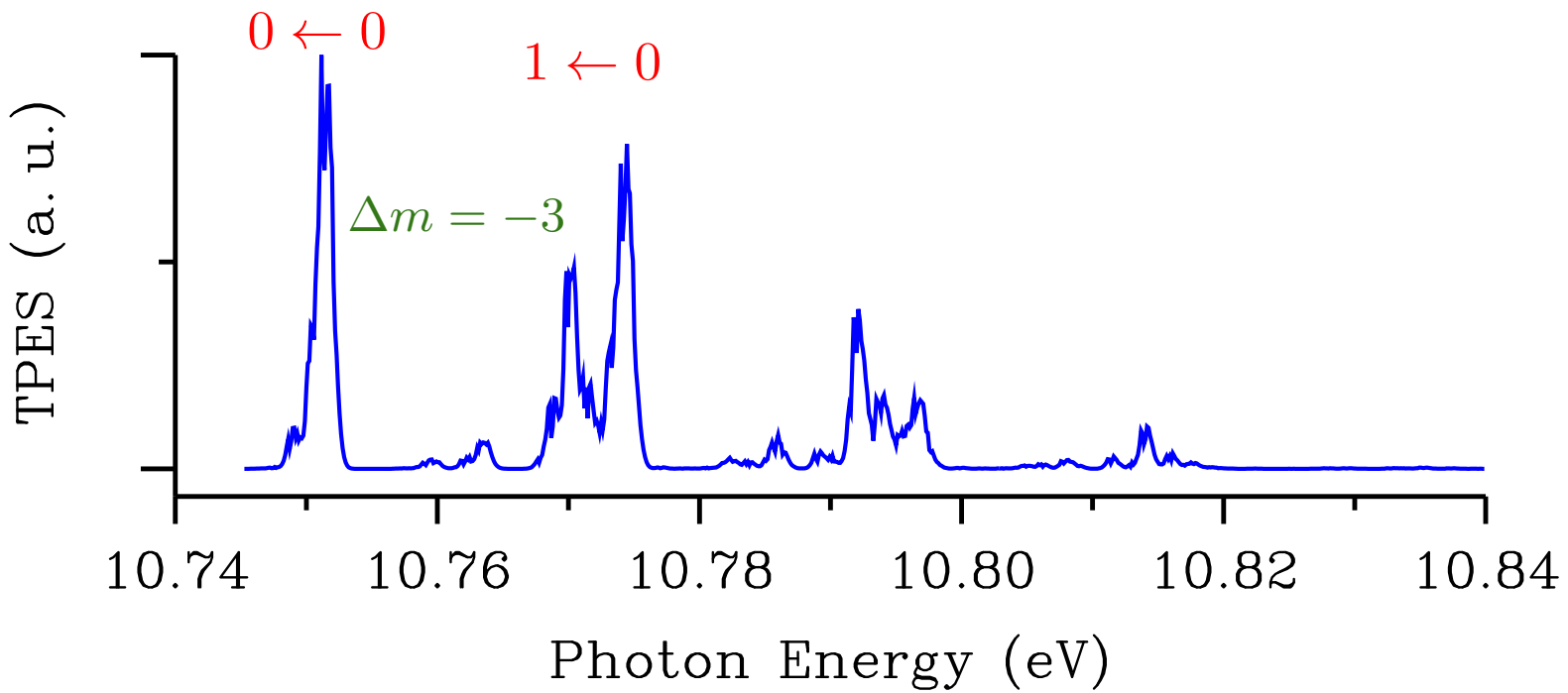

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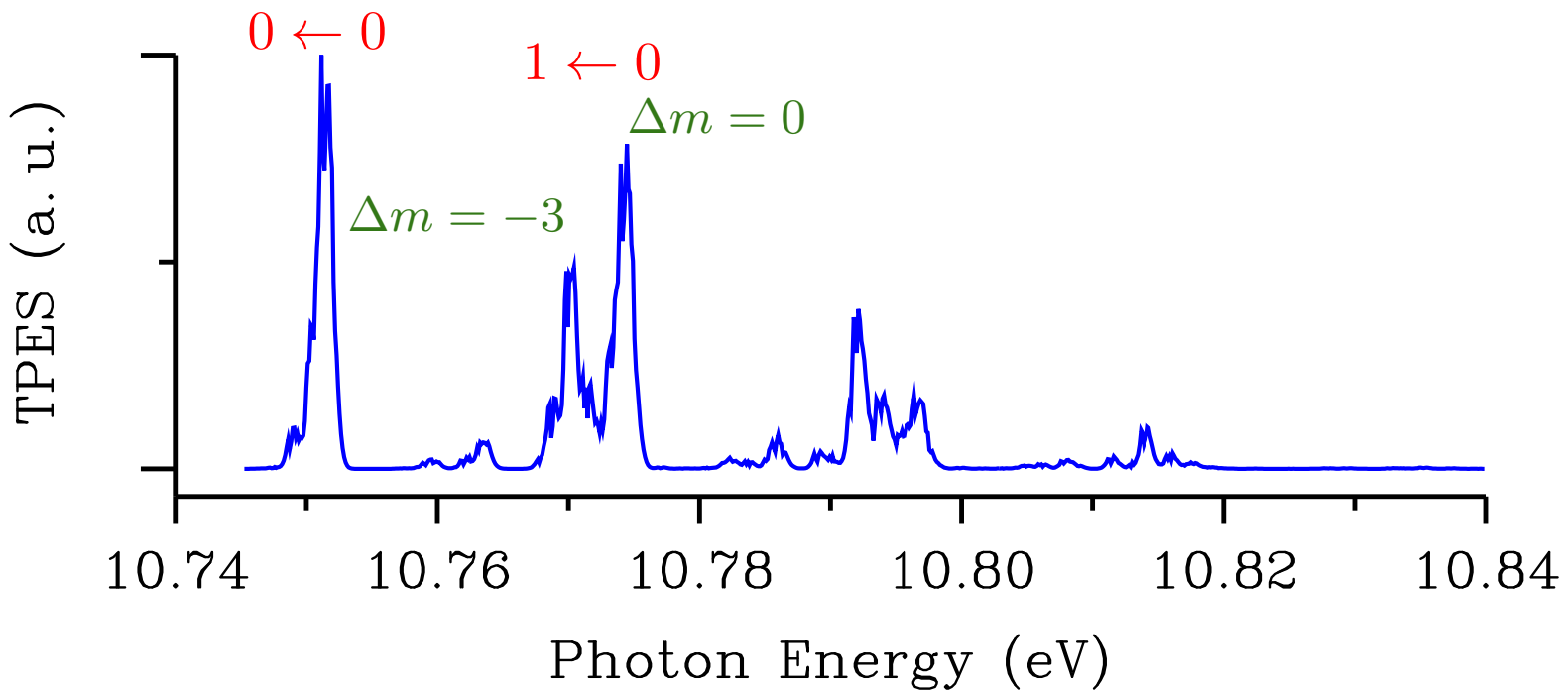

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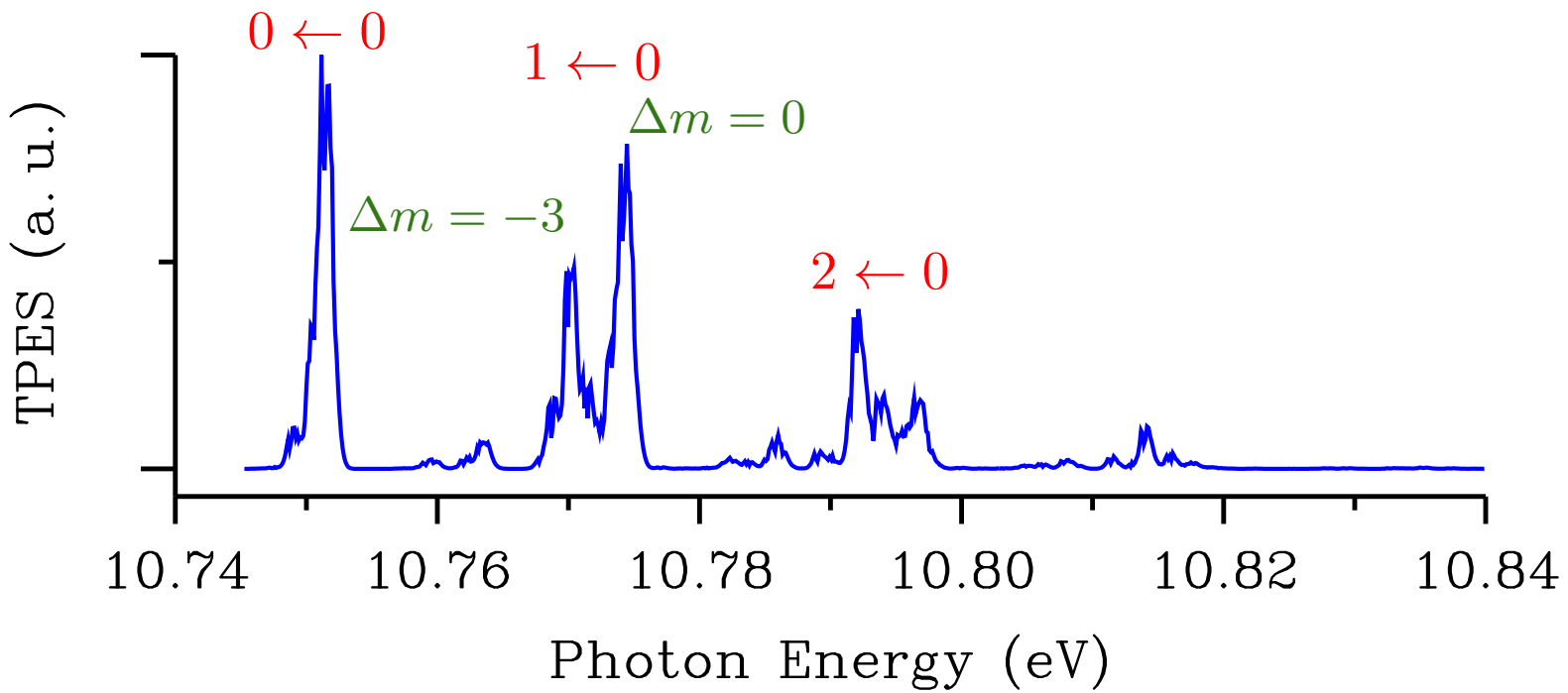

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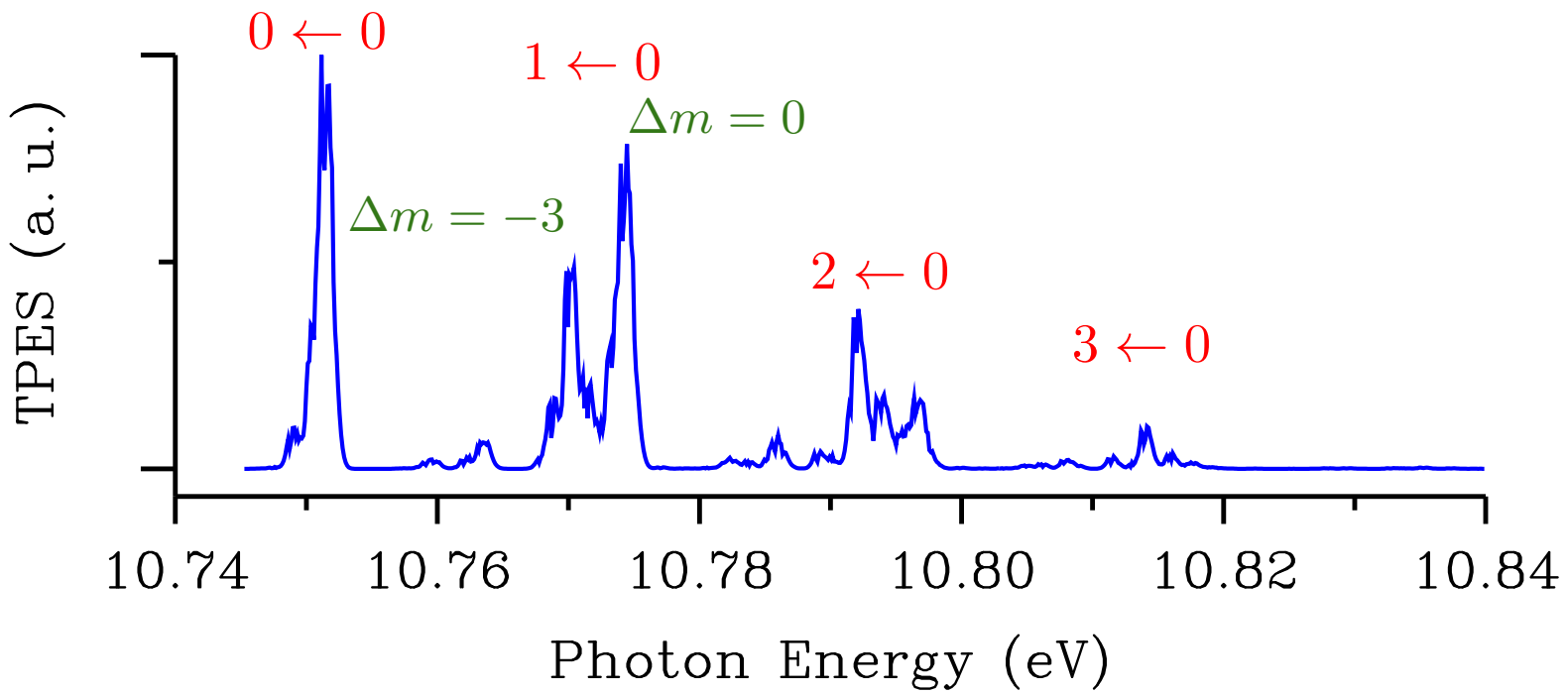

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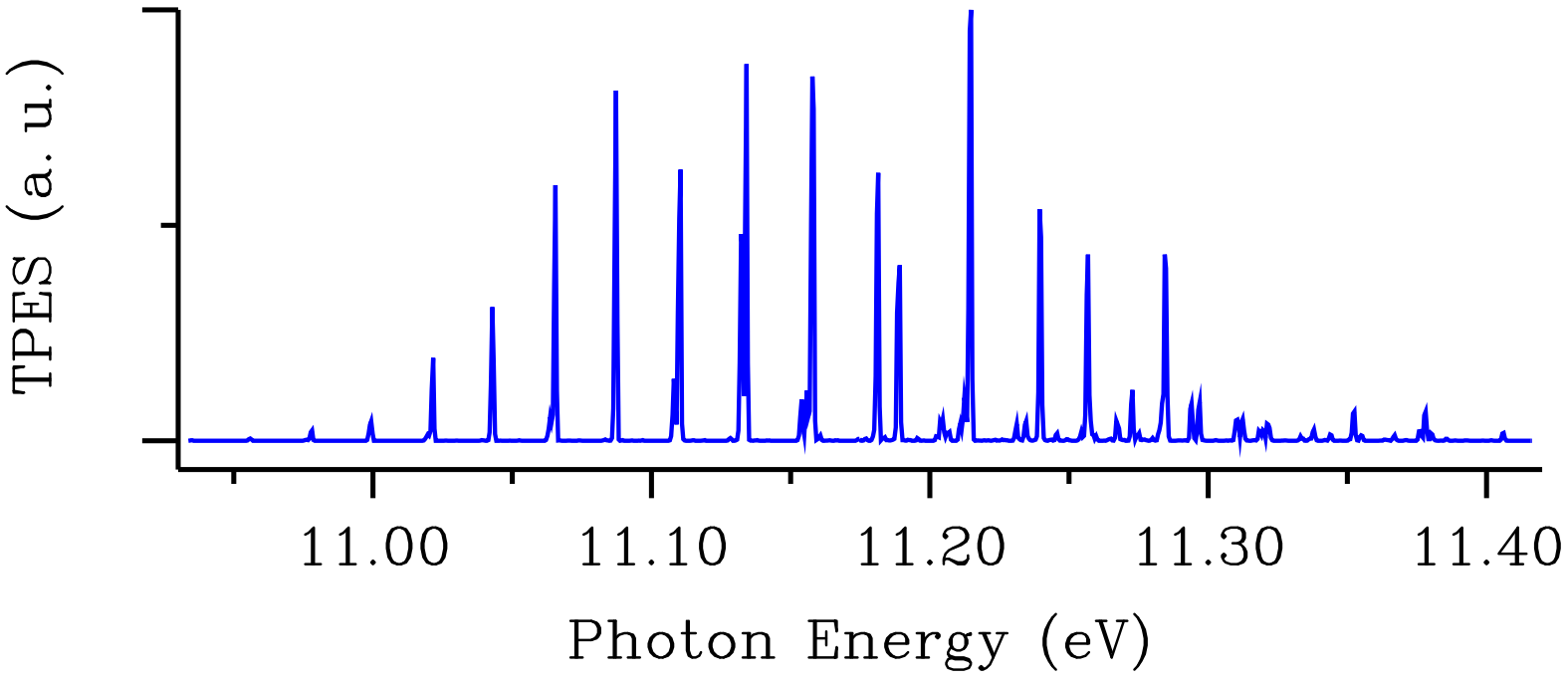

TPES calculation

Franck Condon progressions due to small amplitude vibrational modes involving the NCO group[1,2] should be taken into account

[1] Hirschmann, Kniseley, & Fassel, *Spectrochim. Acta* **21** (1965) 2125

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Mode	$X\,^1A'$	$X^+\,^2A''$
C–N	852	800
ν_s(NCO)	1437	1290
ν_a(NCO)	2288	2150

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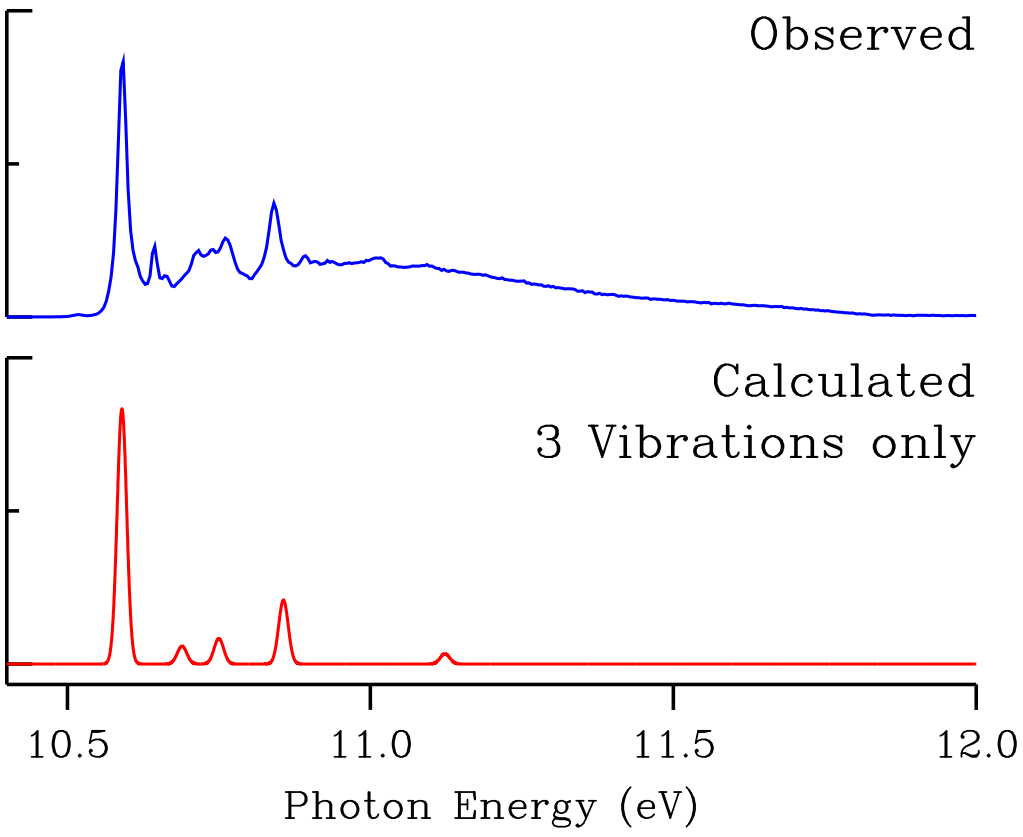
[2] Pasinszki, Vezsprèmi, Fehèr, Kovač, Klasinc, & McGlynn, *Int. J. Qant. Chem.* **26** (1992) 443

Observed and calculated TPES (3 vibrations only)



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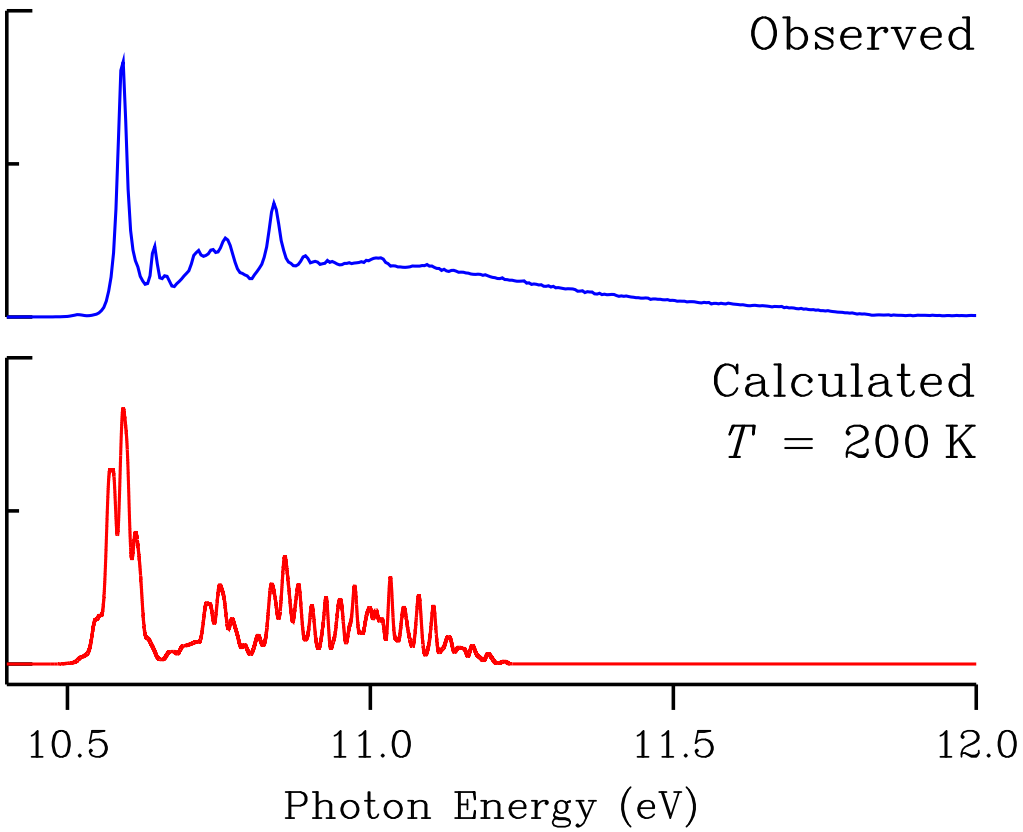

Observed and calculated TPES

Without the Franck Condon progressions due to small amplitude vibrational modes and the $A^+\,{}^2A' \leftarrow X\,{}^1A'$ ionizing transition

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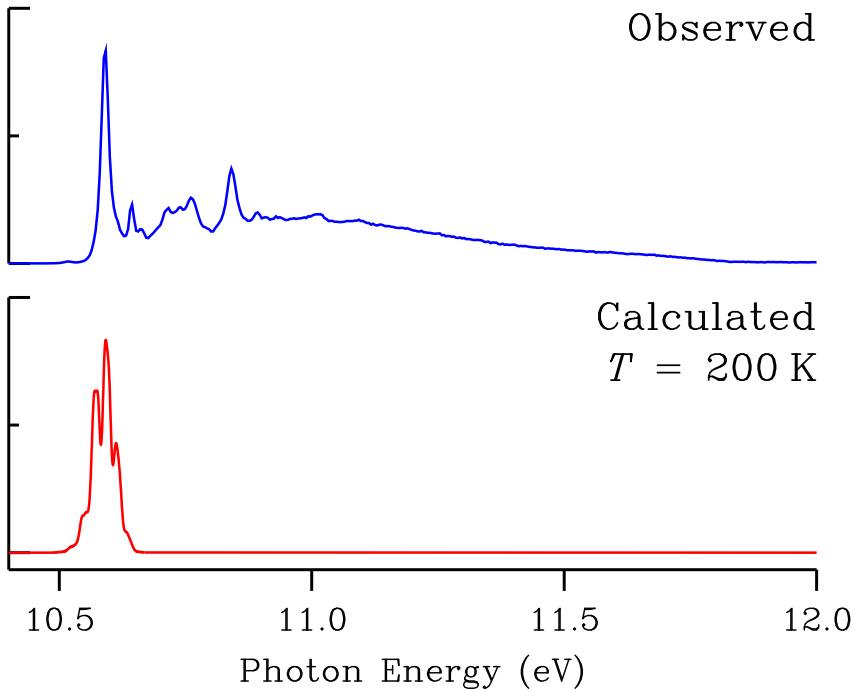

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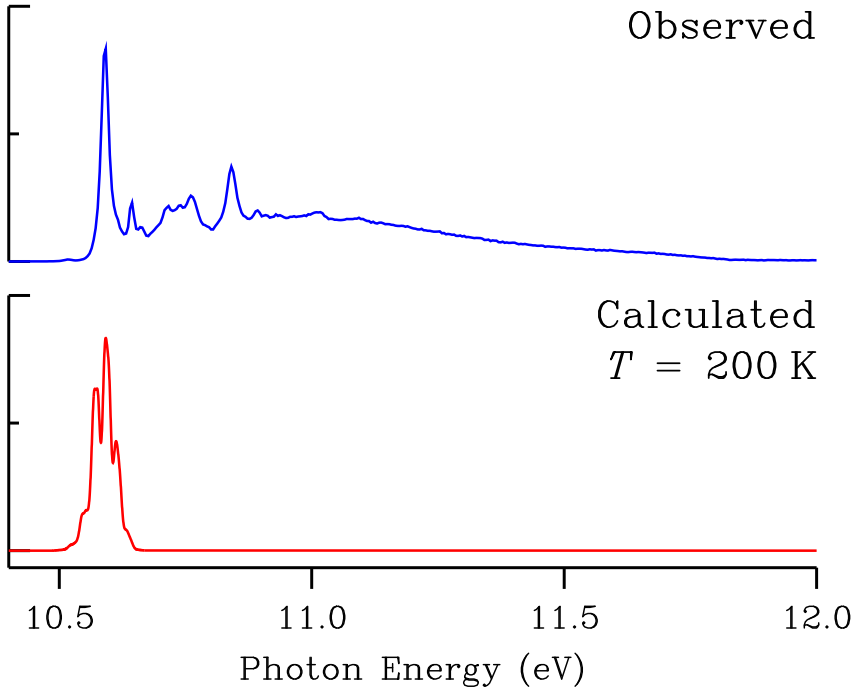

The $X^+\,^2A'' \leftarrow X\,^1A'$ ionizing transition leads to a feature which is either too wide or too narrow

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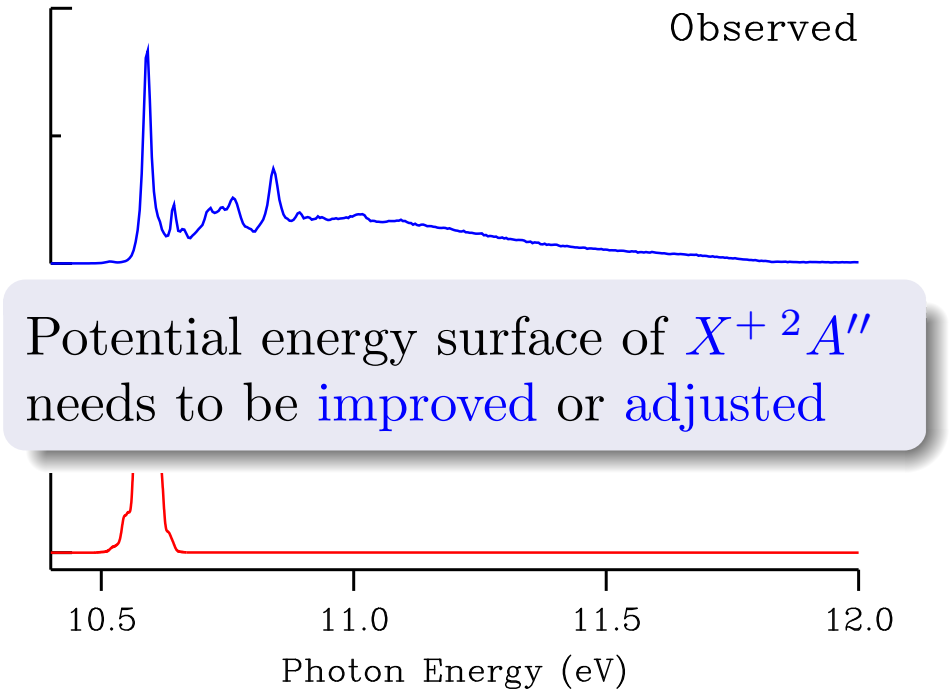

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Thank You