Experimental and theoretical investigations of the threshold photoelectron spectrum of the CH_2 radical

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[b]ISM, Université de Bordeaux, Talence, France
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- Spectroscopic modeling of CH_2 and CH_2^+
- Comparisons bewteen observed and calculated TPES

Previous investigations

[1] Willitsch, Imbach, and F. Merkt, *J. Chem. Phys.* **117** (2002) 1939
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Because CH_2 is an unstable radical, very difficult to produce, almost no results were available concerning its photoelectron spectrum

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A very accurate value of the adiabatic ionizing potential (AIP) was obtained:

$$\text{AIP} = 10.3864 \text{ eV}$$

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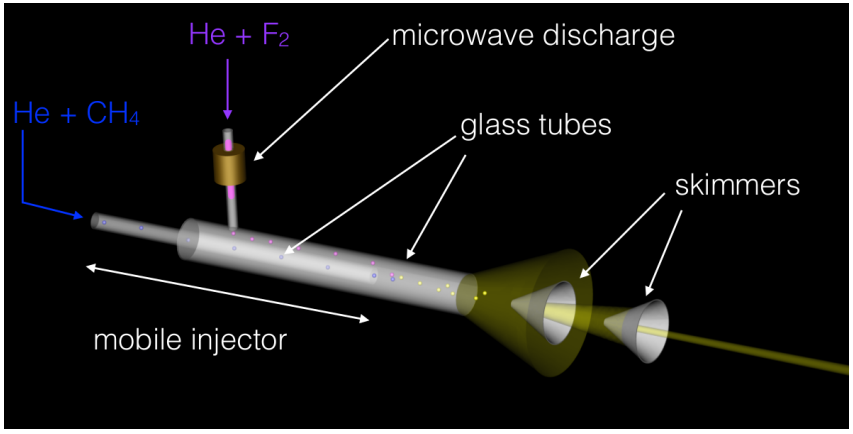

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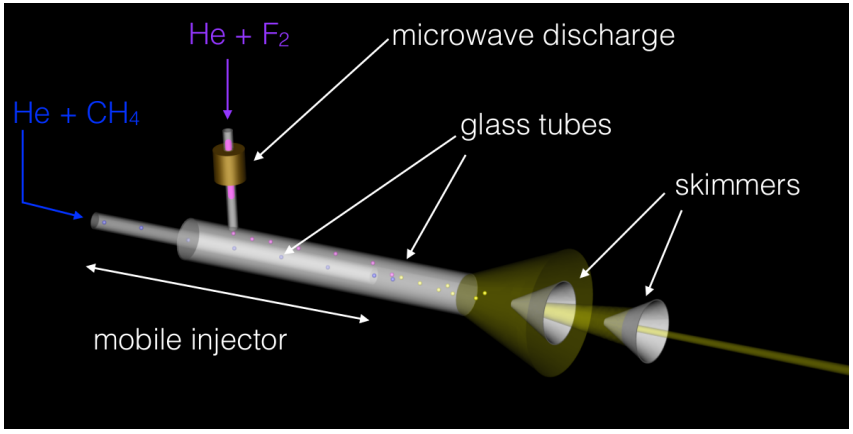

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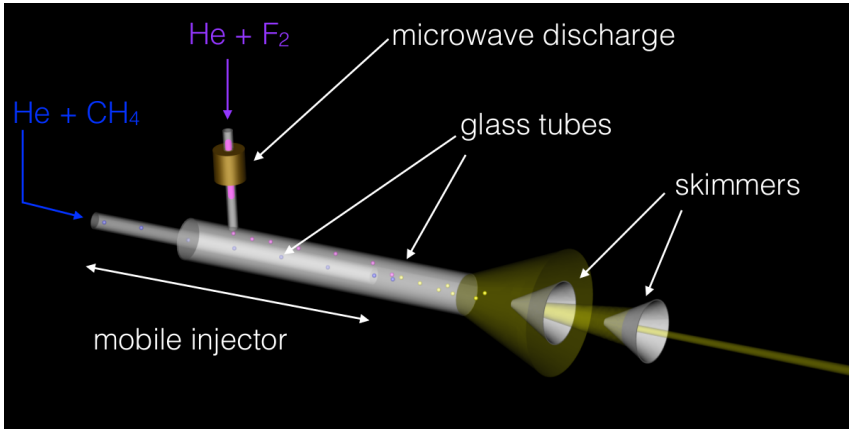

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$$CH_4 + F \longrightarrow CH_3 + HF$$
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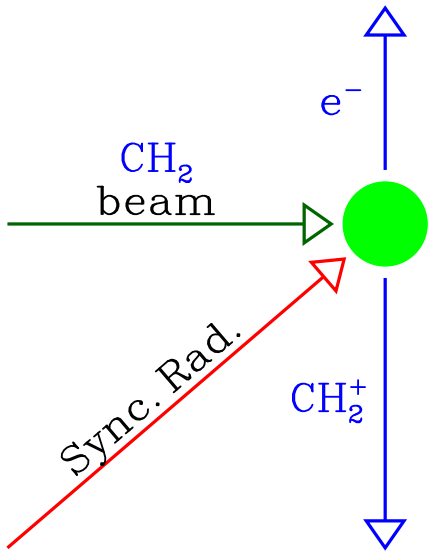

$$CH_2 + h\nu(\mathrm{eV}) \longrightarrow CH_2^+ + e^-$$

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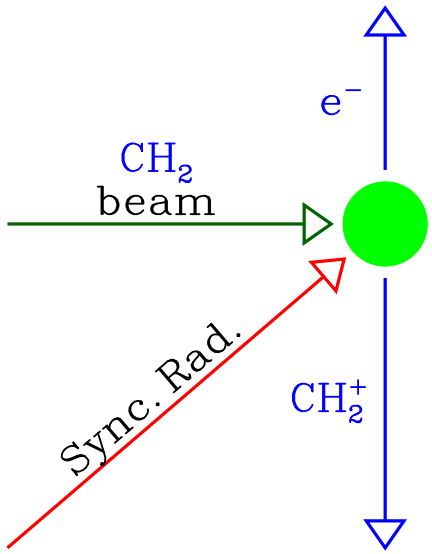

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The e^- signal is monitored

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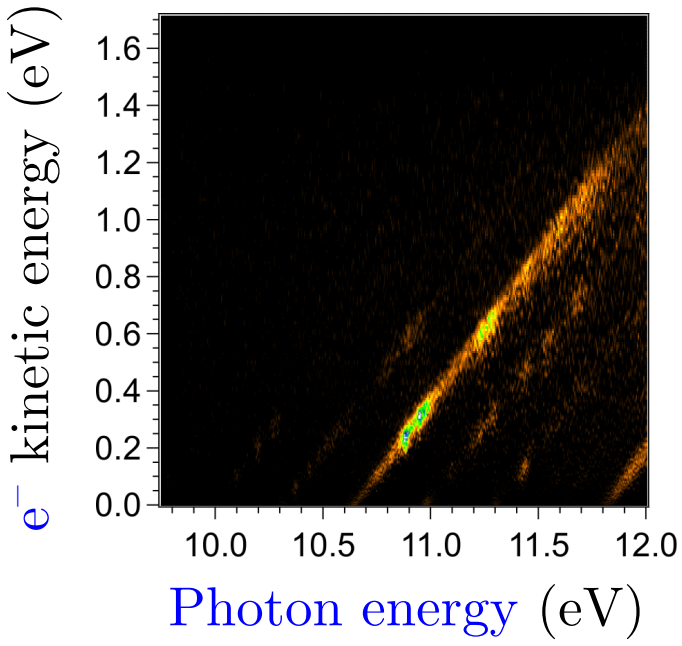

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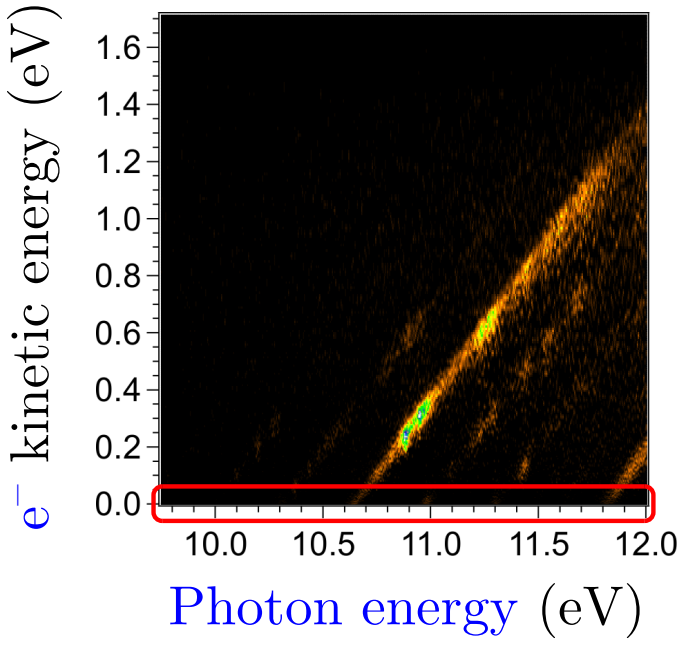

Threshold photoelectron spectrum

e^- with zero kinetic energy

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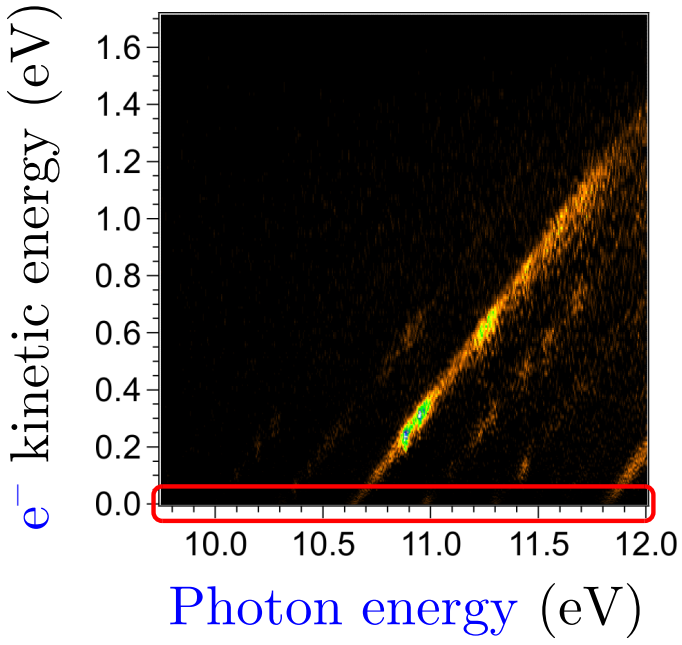

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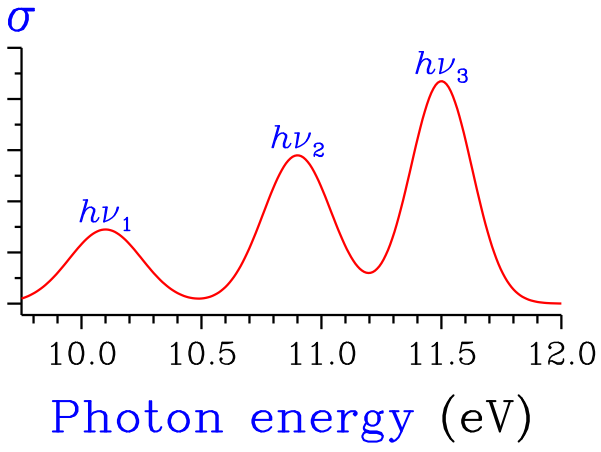

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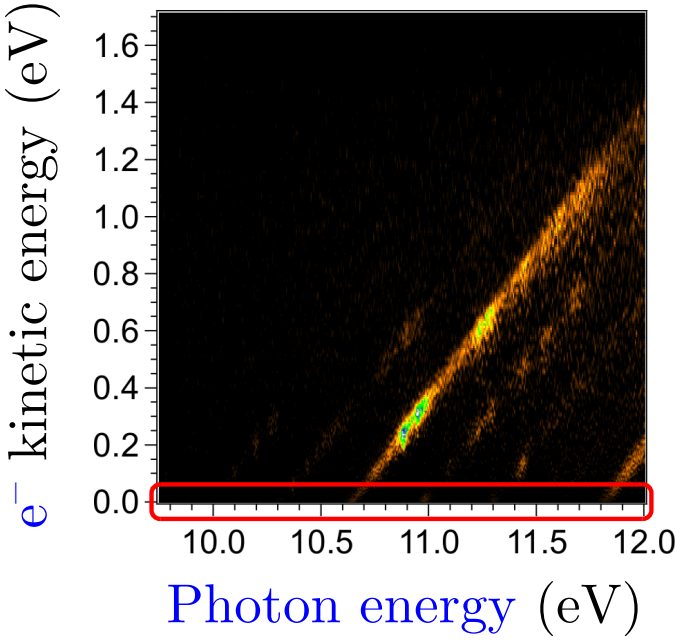

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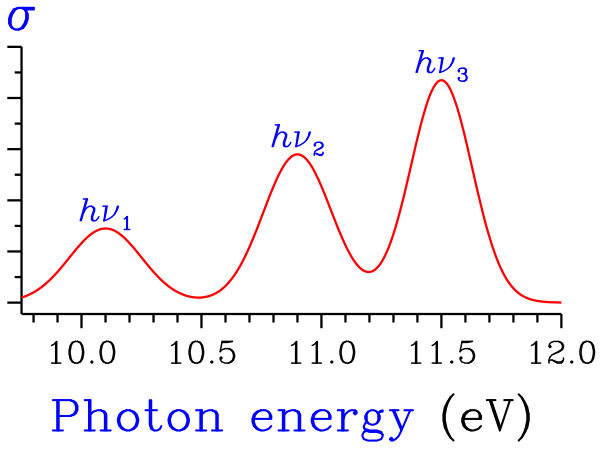

$$h\nu_i = E(CH_2^+) - E(CH_2)$$

Spectroscopy of CH_2 and CH_2^+

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- CH_2^+ is even more difficult to deal with as it displays a strong Renner-Teller effect[4]

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Modeling the threshold photoelectron spectrum

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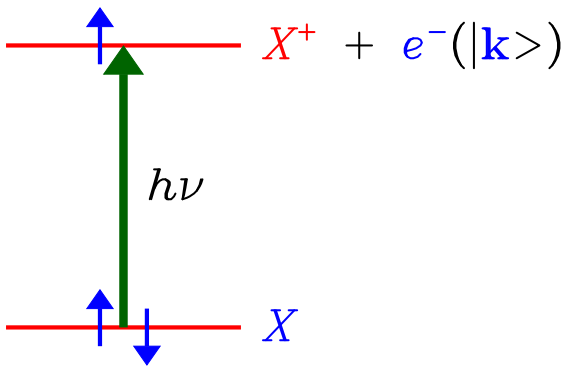

k describes continuum state of e^-

Photoionization cross-section σ is

$$\sum_{\text{Deg. States}} \left| < \mathbf{k}| < X^+ |\mu_Z| X > \right|^2$$

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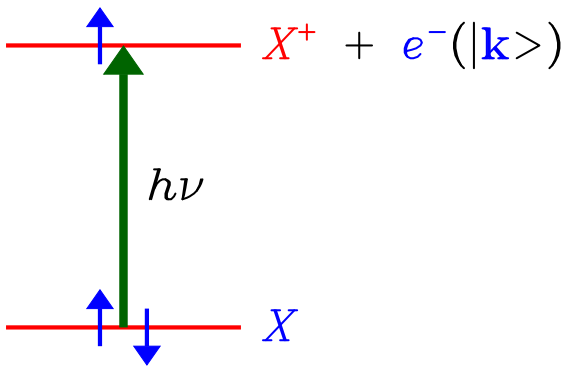

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Expressions were derived for linear molecules[1–4]

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Total photoionization cross-section: asymmetric top

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For $f = |N^+ K_a^+ K_c^+, v^+\rangle |X^+\rangle$ and $g = |N'' K_a'' K_c'', v''\rangle |X\rangle$

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   - Dependence on v^+ and v''
   - Spectroscopy of CH_2 and CH_2^+ must be known

Energy levels of CH_2

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Energy levels of CH_2

Rovibrational energies were calculated[1] using a tridimensional potential energy surface[2]

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(000)	1	0	15.6	15.6		1	1	3066.9	3067.0
	1	1	78.9	78.9	(001)	0	0	3213.5	3213.6
(010)	0	0	963.1	963.4		1	0	3228.9	3229.0
	1	0	978.6	978.9		1	1	3286.0	3286.2
	1	1	1132.7	1132.7	(110)	0	0	3957.8	3949.7
(020)	0	0	1828.5	1829.0		1	0	3973.1	3965.1
	1	0	1943.9	1844.5		1	1	4120.1	4120.2
	1	1	2195.5	2195.6	(040)	0	0	4000.0	4006.7
(030)	0	0	2818.8	2818.2		1	0	4015.8	4022.6
	1	0	2834.5	2834.0		1	1	4614.3	4614.3
	1	1	3349.6	3349.5	(011)	0	0	4193.2	4192.8
(100)	0	0	2992.0	2992.3		1	0	4208.4	4208.1
	1	0	3007.4	3007.7		1	1	4337.8	4337.9

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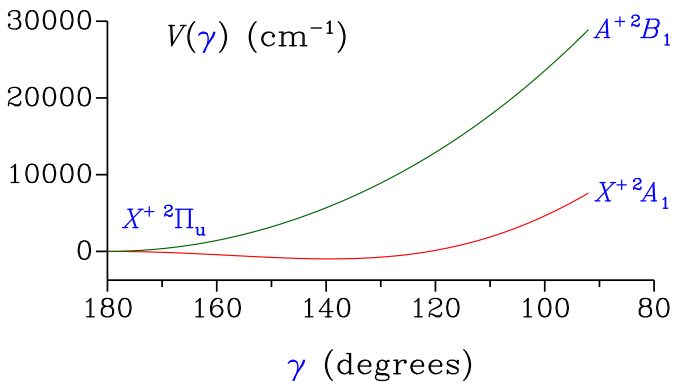

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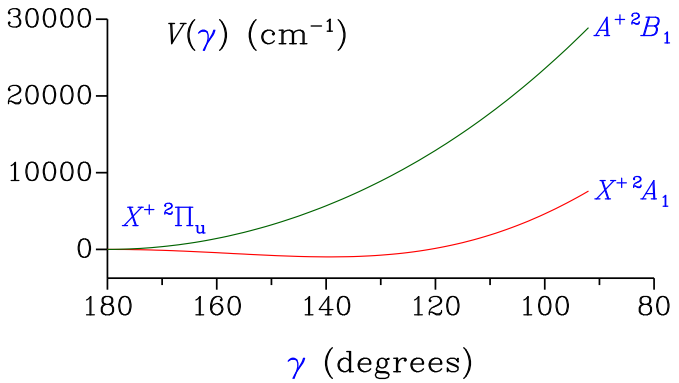

Tridimensional potential energy surfaces for $X^+ {}^2A_1$ and $A^+ {}^2B_1$ electronic substates were used.[3,4]

[1] Gutlé and Coudert, *J. Molec. Spectrosc.* **273** (2012) 44
[2] Mitrushchenkov, *J. Chem. Phys.* **136** (2012) 024108
[3] Kraemer, Jensen, and Bunker, *Can. J. Phys.* **72** (1994) 871
[4] Jensen, Brumm, Kraemer, and Bunker, *J. Molec. Spectrosc.* **172** (1995) 194

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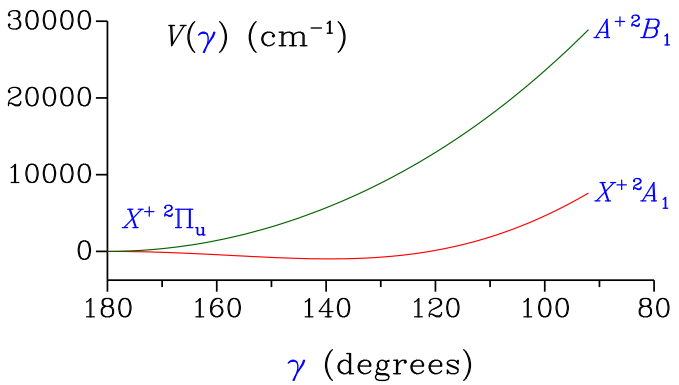

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Energies in *this work* are within 5 cm^{-1} from those of Jensen *et al.*[4]

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[1] Gutlé and Coudert, *J. Molec. Spectrosc.* **273** (2012) 44
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[3] Kraemer, Jensen, and Bunker, *Can. J. Phys.* **72** (1994) 871
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Energy levels of CH_2^+

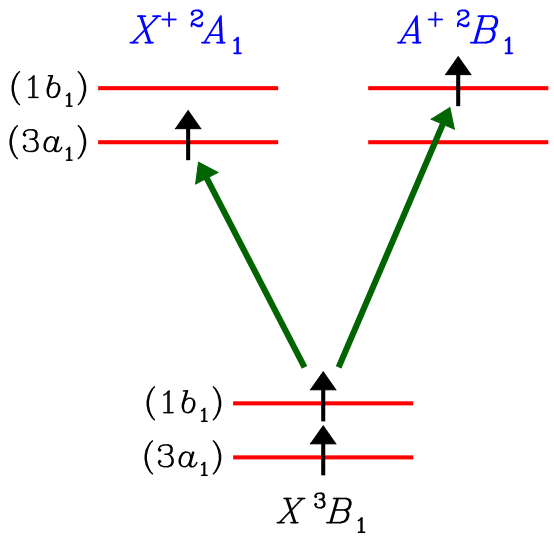
[1] Jensen, Brumm, Kraemer, and Bunker, *J. Molec. Spectrosc.* **172** (1995) 194

Energy levels of CH_2^+

State	v	Cal[1]	*This work*	State	v	Cal[1]	*This work*
$X^+\,^2A_1$	(010)	995.6	995.7	$X^+\,^2A_1$	(021)	5176.8	5178.7
	(020)	2093.1	2093.2		(200)	5735.5	5733.9
	(100)	2899.5	2898.9		(101)	5922.0	5921.5
	(001)	3131.4	3131.9		(050)	6082.2	6082.7
	(030)	3327.1	3327.2		(002)	6203.6	6205.0
	(110)	3886.9	3886.1		(130)	6222.1	6223.2
	(011)	4109.5	4110.7		(031)	6375.0	6377.8
	(040)	4672.2	4672.3		(210)	6712.4	6712.4
	(120)	4974.7	4975.4		(111)	6890.2	6891.4
$A^+\,^2B_1$	(000)	2980.1	2980.7	$A^+\,^2B_1$	(200)	8689.2	8692.5
	(010)	5350.0	5350.6		(101)	8906.2	8909.7
	(100)	5866.3	5867.9		(002)	9219.9	9223.4
	(001)	6130.2	6131.8		(030)	10028.4	10029.5
	(020)	7699.1	7699.9		(120)	10536.1	10537.0
	(110)	8212.3	8215.2		(021)	10736.8	10740.7
	(011)	8443.9	8446.7				

[1] Jensen, Brumm, Kraemer, and Bunker, *J. Molec. Spectrosc.* **172** (1995) 194

Actual cross-section calculation



For $X^+\,^2A_1 \leftarrow X\,^3B_1$ transitions:

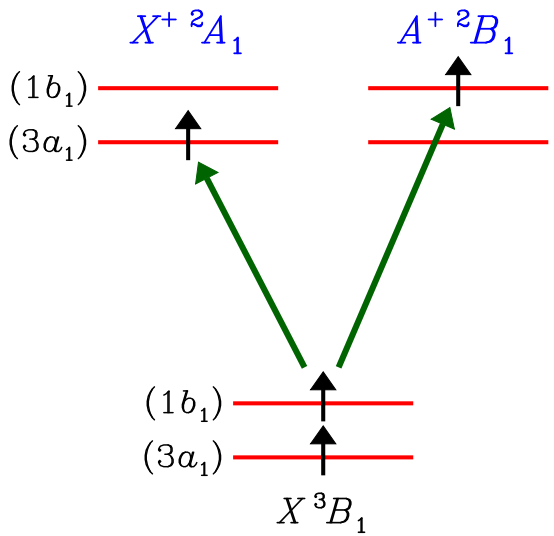
$$\sigma_{\text{tot}} \propto (q_v^{1a_1})^2 \times Q^{1a_1}(l'') \times B^{(g)}_{l''\lambda''}$$

For $A^+\,^2B_1 \leftarrow X\,^3B_1$ transitions:

$$\sigma_{\text{tot}} \propto (q_v^{3b_1})^2 \times Q^{3b_1}(l'') \times B^{(g)}_{l''\lambda''}$$

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

Actual cross-section calculation



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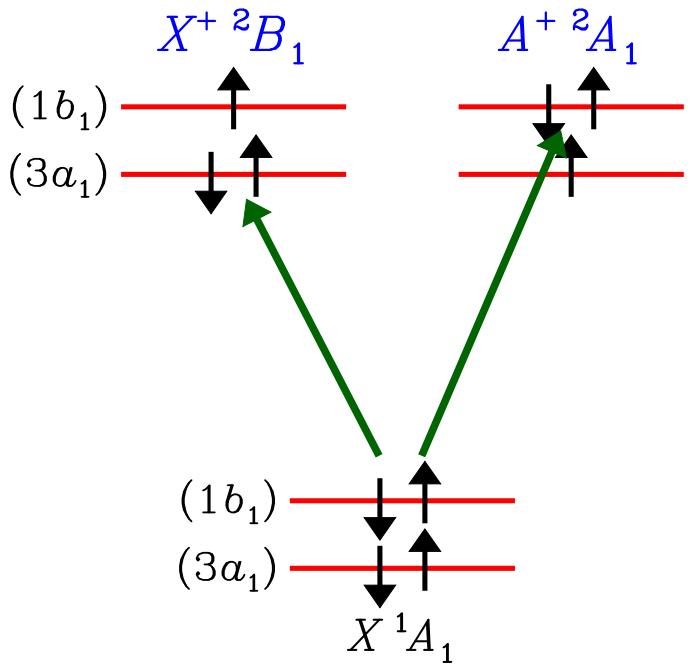
$$\begin{cases} (q_v^{1a_1})^2,\ Q^{1a_1}(l'') \\ (q_v^{3b_1})^2,\ Q^{3b_1}(l'') \end{cases}$$ from energy level calculation

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

H_2O as a test case

Ground $^2\Pi_u$ electronic state of H_2O^+ split into $\begin{cases} X^+\,^2B_1 \\ A^+\,^2A_1 \end{cases}$



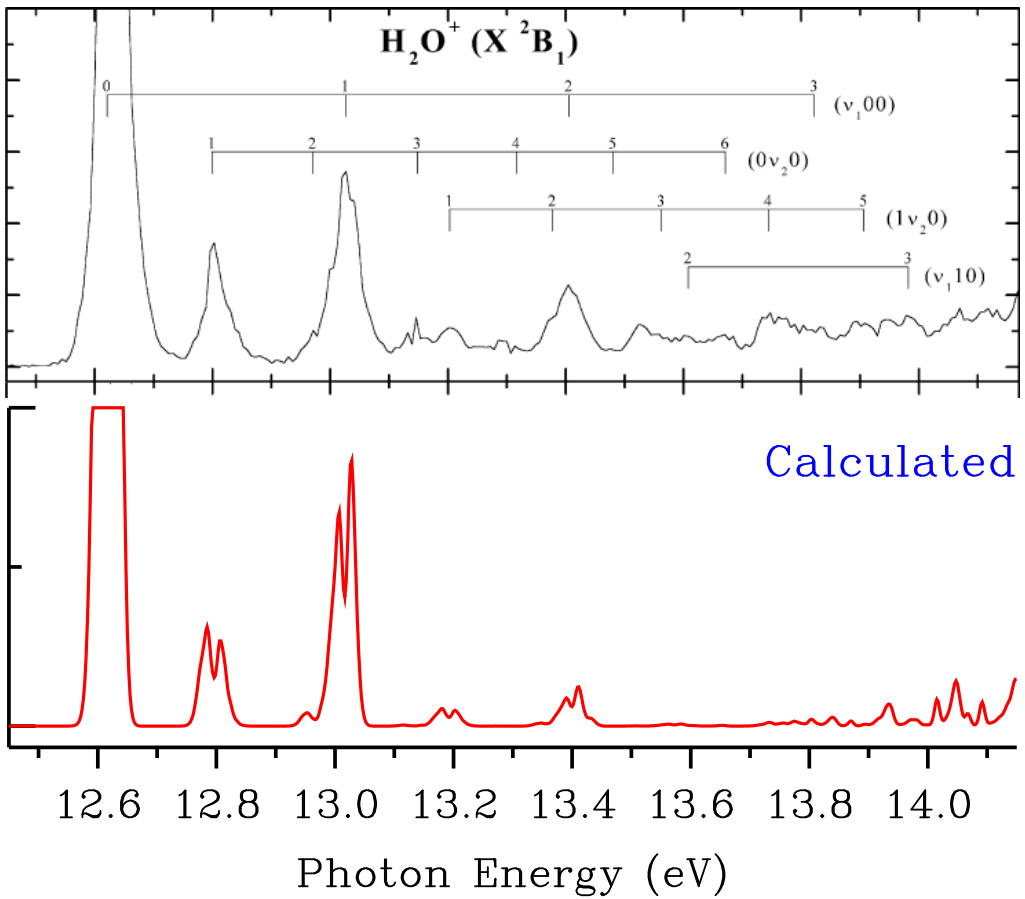
[1] Partridge and Schwenke, *J. Chem. Phys.* **106** (1997) 4618

[2] Wu, Chen, Yang, Guo, Liu, Li, J. Buenker, and P. Jensen, *J. Molec. Spectrosc.* **225** (2004) 96

[3] Truong, Yencha, Juarez, Cavanagh, Bolognesi & King, *Chem. Phys.* **355** (2009) 183

TPES of H_2O

Observed[1] vs. calculated TPES of H_2O for the $X^+\,^2B_1 \leftarrow X\,^1A_1$ ionizing transition



[1] Truong, Yencha, Juarez, Cavanagh, Bolognesi & King, *Chem. Phys.* **355** (2009) 183

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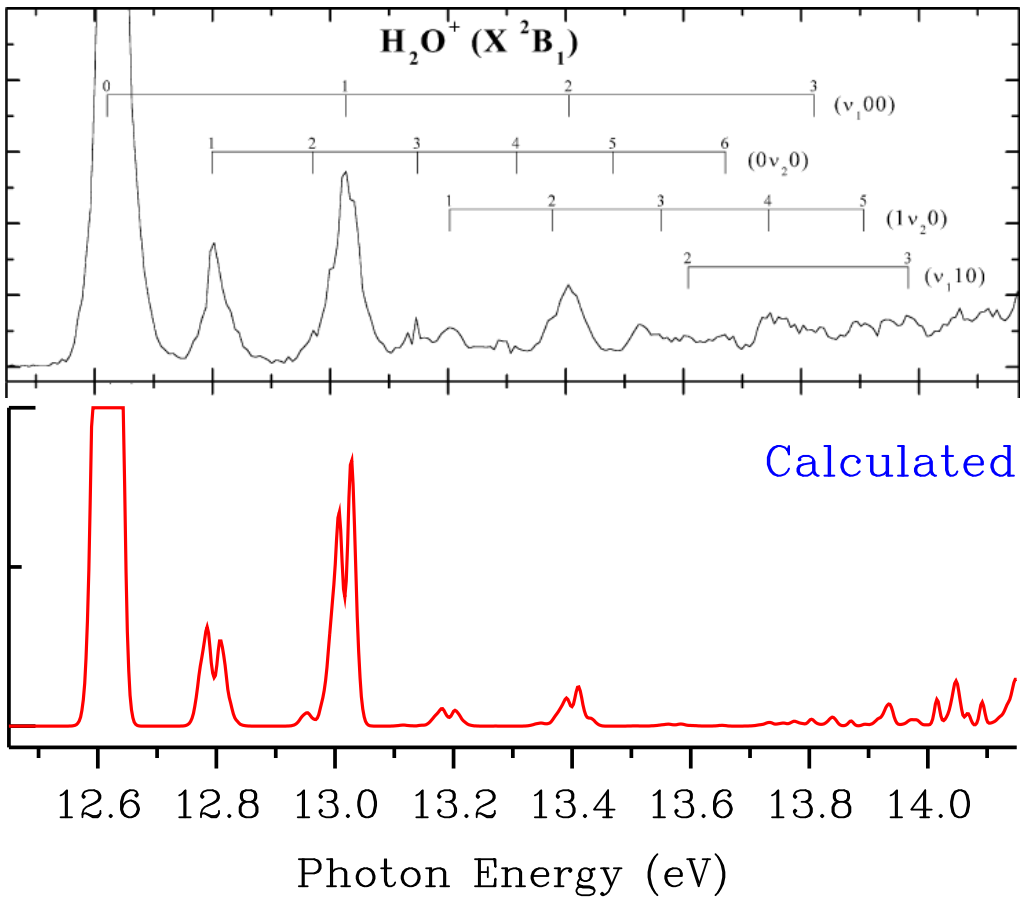

$T = 100$ K
hwhm $= 40$ cm^{-1}

[1] Truong, Yencha, Juarez, Cavanagh, Bolognesi & King, *Chem. Phys.* **355** (2009) 183

TPES of H_2O

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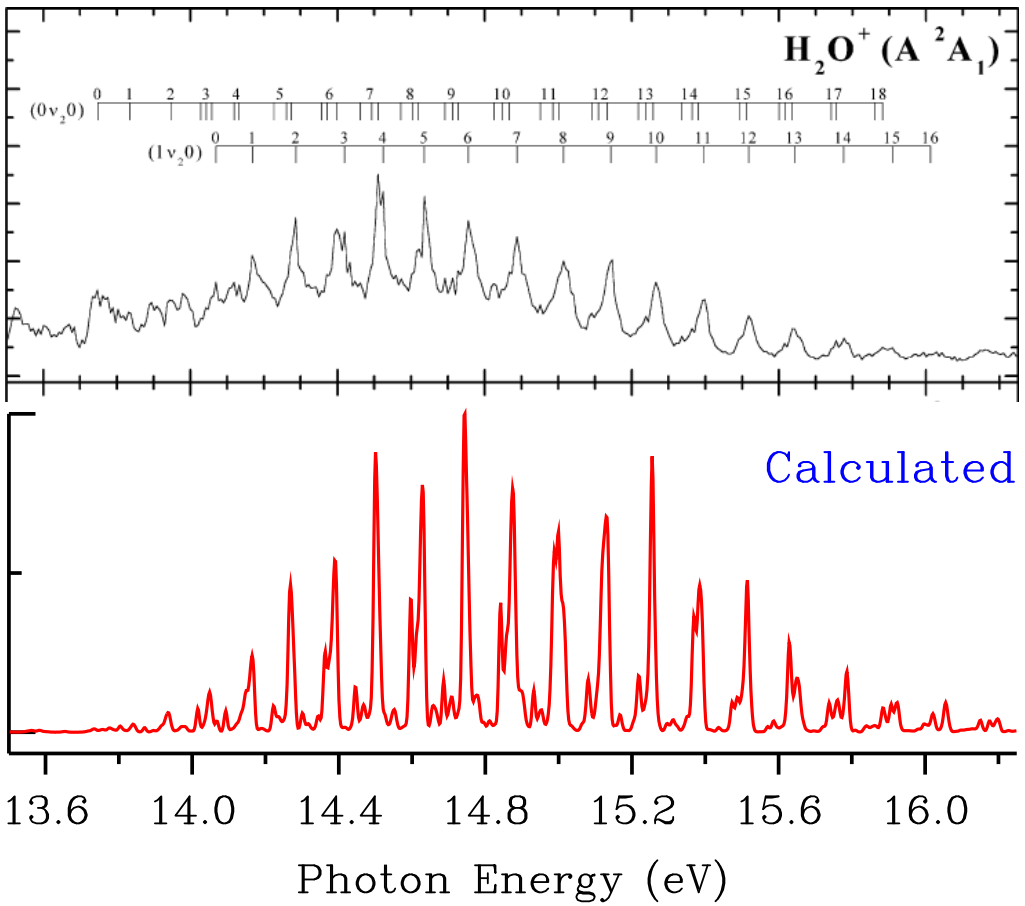

[1] Truong, Yencha, Juarez, Cavanagh, Bolognesi & King, *Chem. Phys.* **355** (2009) 183

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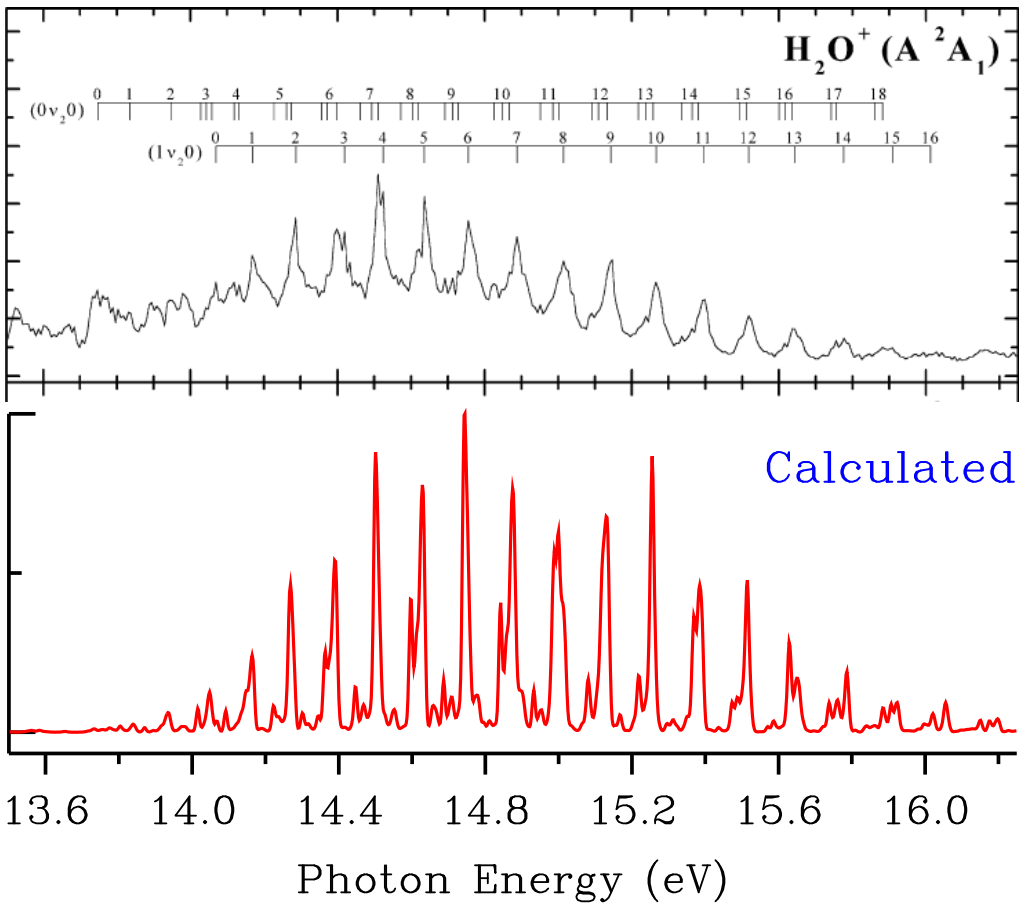

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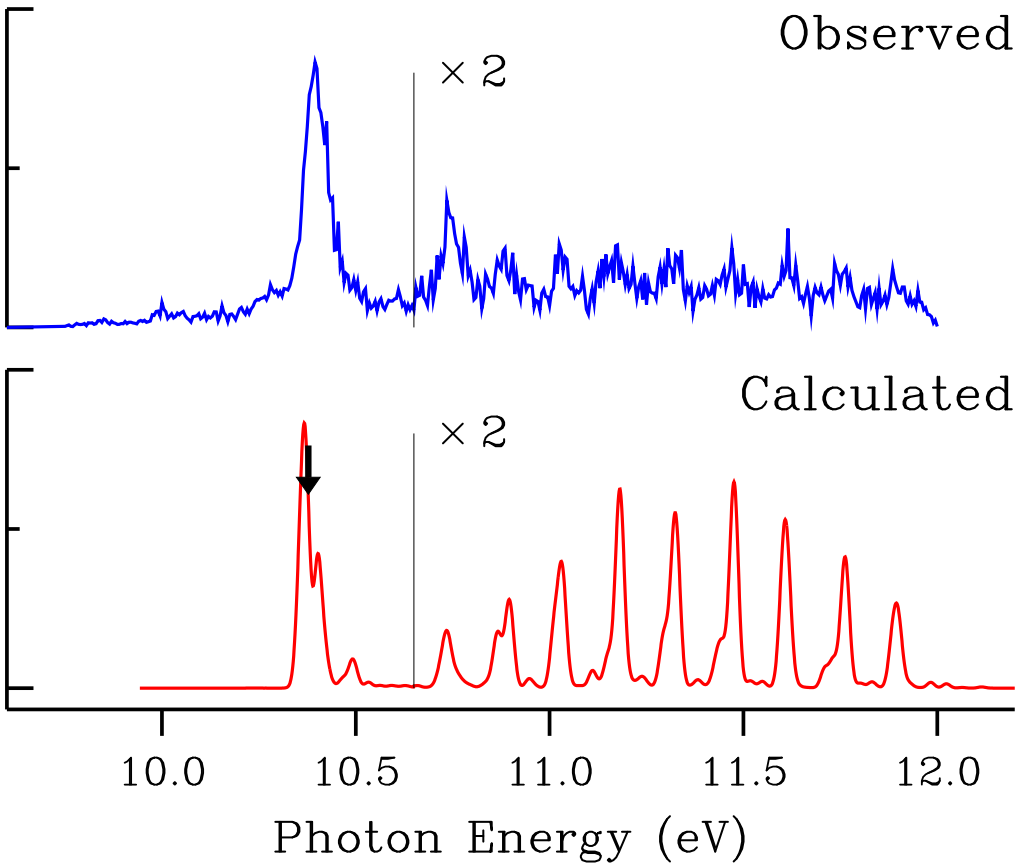
[1] Truong, Yencha, Juarez, Cavanagh, Bolognesi & King, *Chem. Phys.* **355** (2009) 183

TPES of CH_2

Observed vs. calculated TPES of CH_2



[1] Willitsch, Imbach, and F. Merkt, *J. Chem. Phys.* **117** (2002) 1939
[2] Willitsch and Merkt, *J. Chem. Phys.* **118** (2003) 2235

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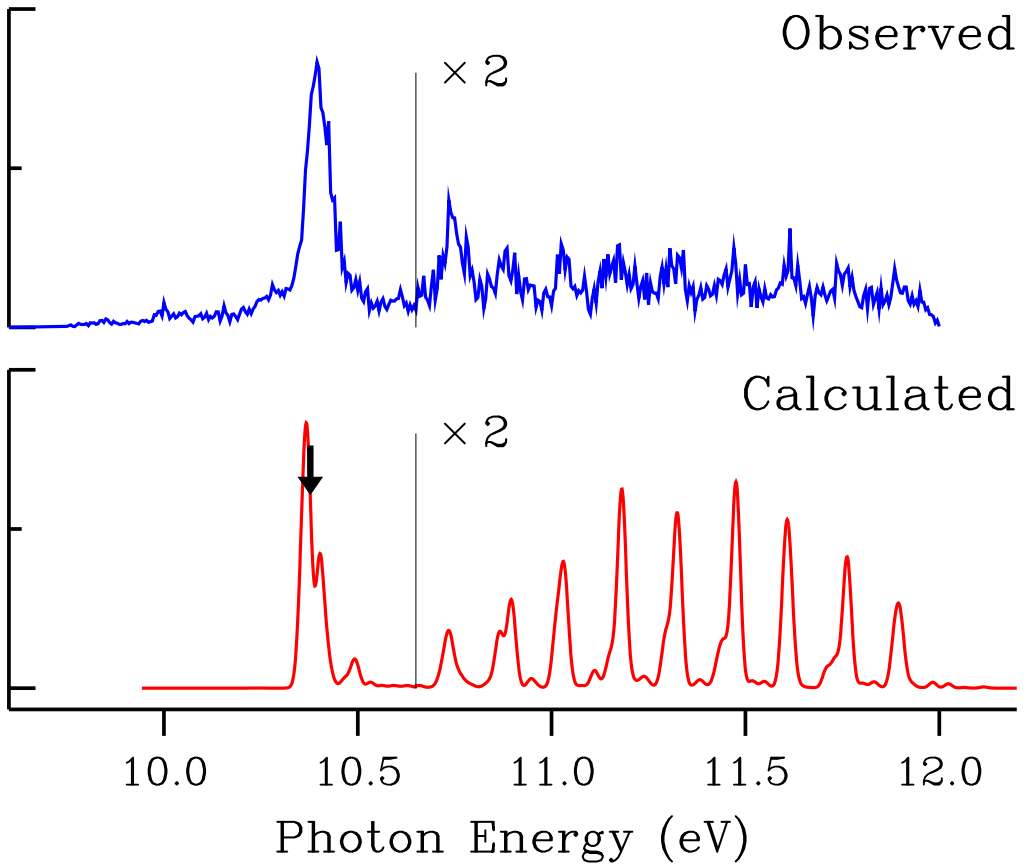

$T = 300$ K

hwhm $= 90$ cm^{-1}

[1] Willitsch, Imbach, and F. Merkt, *J. Chem. Phys.* **117** (2002) 1939

[2] Willitsch and Merkt, *J. Chem. Phys.* **118** (2003) 2235

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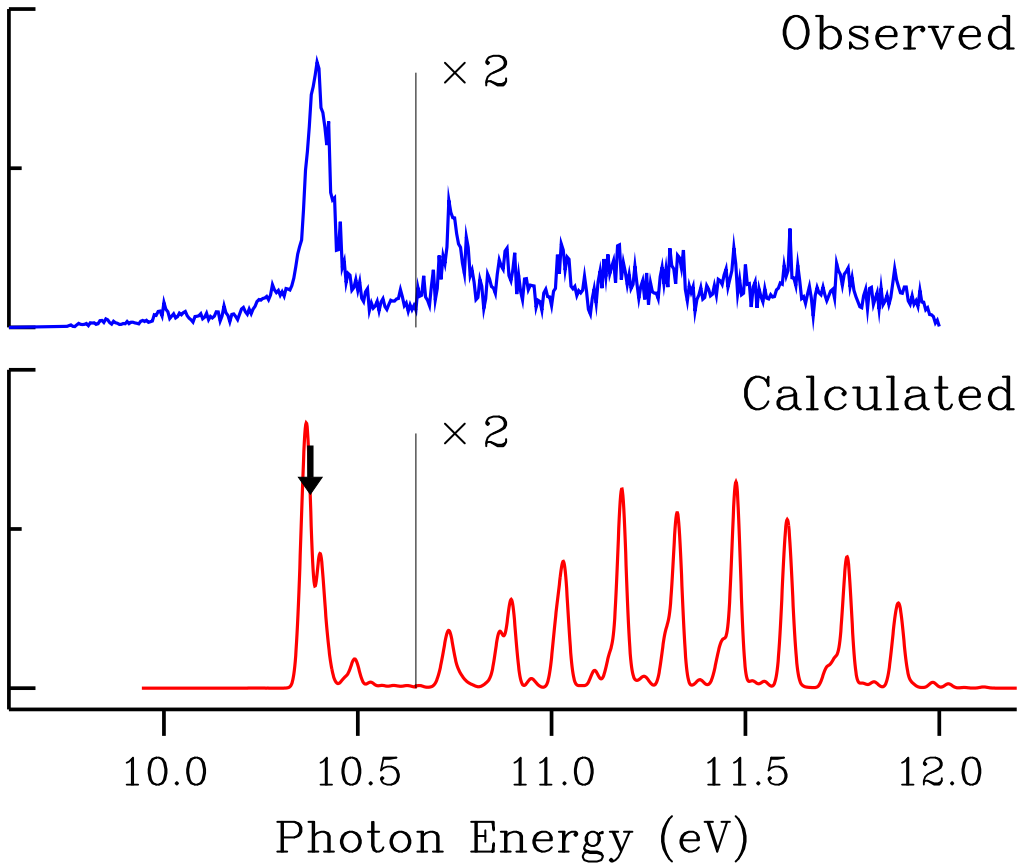

$T = 300$ K

hwhm $= 90$ cm^{-1}

AIP $= 10.378$ eV

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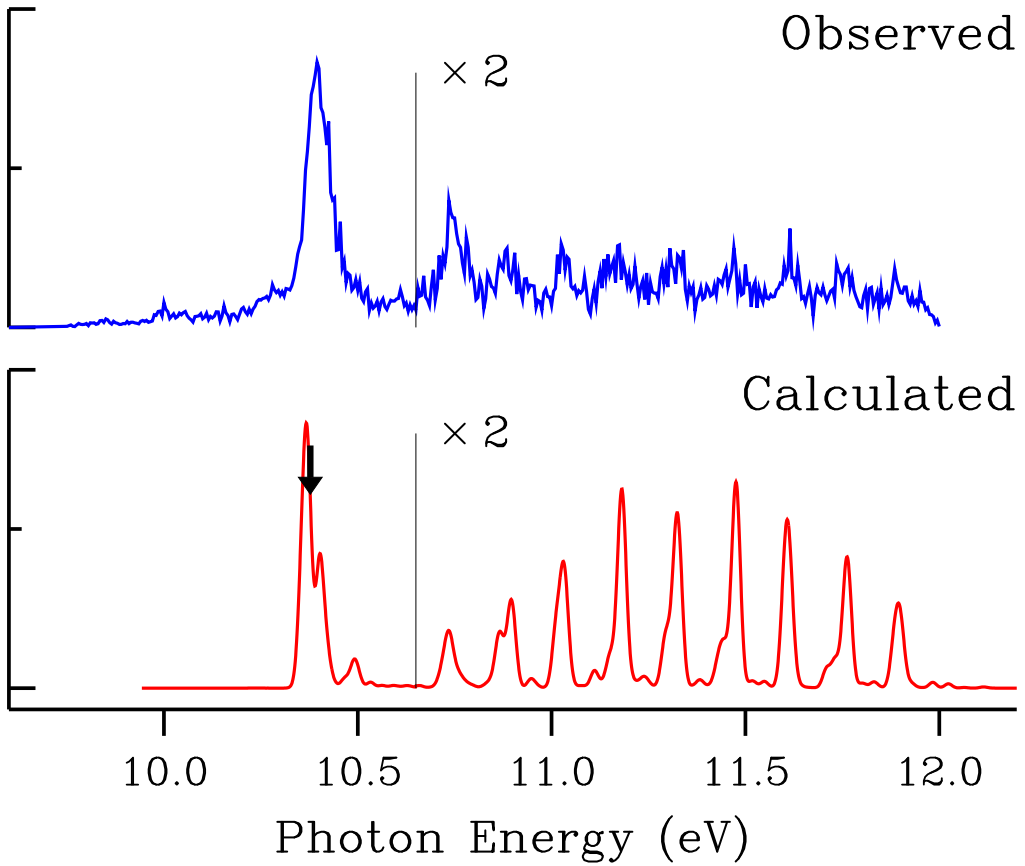

$T = 300$ K

hwhm $= 90$ cm^{-1}

AIP $= 10.378$ eV

$= 10.3864$ eV

[1] Willitsch, Imbach, and F. Merkt, *J. Chem. Phys.* **117** (2002) 1939

[2] Willitsch and Merkt, *J. Chem. Phys.* **118** (2003) 2235

Thank You