

Ab initio calculations for photodissociation of diatomic molecules

Gerrit C. Groenenboom

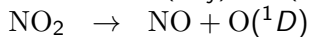
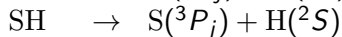
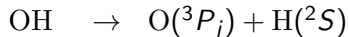
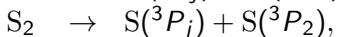
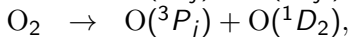
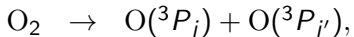
Theoretical Chemistry
Institute for Molecules and Materials
Radboud University Nijmegen
The Netherlands

Leiden 2015

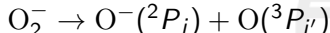


Experimental collaborators on photodissociation

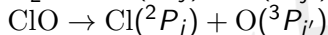
Dave Parker (Nijmegen):



Wim van der Zande (Nijmegen):



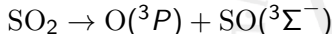
Simon North (Texas A&M):



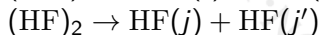
Maurice Janssen (VU):



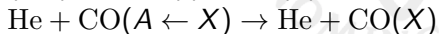
Mark Brouard (Oxford):



Roger Miller (North Carolina):

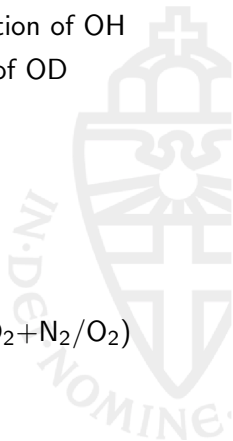


Gerard Meijer (Nijmegen):

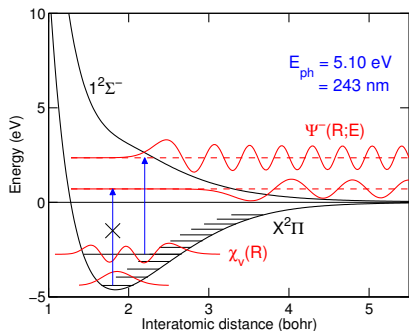


www.theochem.ru.nl/cgi-bin/dbase/search.cgi?pr:photo

- Single channel photodissociation - direct dissociation of OH
- Multichannel photodissociation - predissociation of OD
- Correlated fine structure distributions - ClO
 - Adiabatic model
 - Diabatic model
 - Multichannel treatment
- Absolute cross sections:
 - Forbidden transitions, Herzberg I, O₂
- Collision induced absorption, H₂+H₂, N₂+N₂, (O₂+N₂/O₂)



Direct dissociation: $\text{OH}(X^2\Pi) \rightarrow \text{O}(^3P) + \text{H}$



Bound state wave function:

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_X(R) - E_\nu \right] \chi_\nu(R) = 0$$

Continuum wave function:

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_1(R) - E \right] \Psi^-(R; E) = 0$$

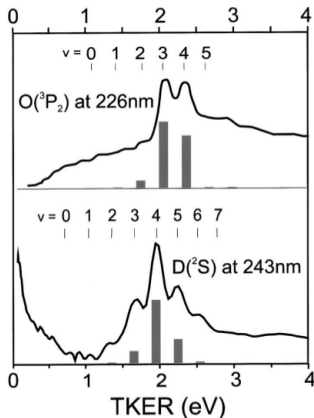
Transition dipole moment:

$$\mu(R) = \langle 1^2\Sigma^- | \hat{\mu}_x | X^2\Pi_x \rangle$$

Photodissociation cross section for $\hbar\omega = E - E_\nu$:

$$\sigma(\omega) = \frac{\pi\omega}{\epsilon_0 c} |\langle \Psi^-(R; E) | \mu(R) | \chi_\nu(R) \rangle|^2$$

Direct dissociation $\text{OD}(X^2\Pi) \rightarrow \text{O}(^3P) + \text{D}(^2S)$



Experiment

- Velocity map ion imaging
- Measure kinetic energy of O or D
- OD produced in discharge
- $T_{\text{rot}} \approx 10\text{K}$

Populations of vibrational level:

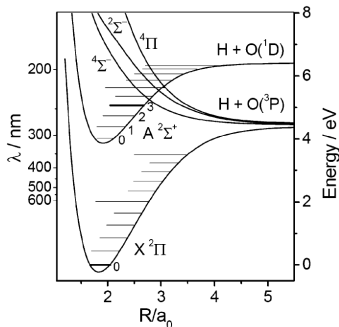
$$P_\nu(T) \propto e^{-E_\nu/kT_{\text{vib}}}$$

Fit to theory: $T_{\text{vib}} \approx 1700\text{K}$

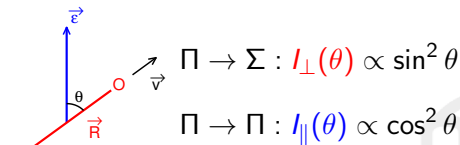
Radenović, van Roij, Chestakov, Eppink, ter Meulen, Parker, Loo, Groenenboom, Greenslade, Lester, J. Chem.

Phys. **119**, 9341 (2003)

Predissociation, $\text{OH}(X^2\Pi) \rightarrow \text{O}(^3P) + \text{H}(^2S)$



Velocity-map ion imaging experiment:



General: $I(\theta) \propto 1 + \beta P_2(\cos \theta)$

$$\beta_{\perp} = -1 \quad \beta_{\parallel} = 2.$$

REMPI detection of fine structure states: $\text{O}(^2P_J, J = 2, 1, 0)$

Further complication, product alignment: $|JM\rangle, M = -J, \dots, J$

$$I_J(\theta, \omega) \propto 1 + \beta_J(\omega) P_2(\cos \theta) + \gamma_J(\omega) P_4(\cos \theta)$$

Molecular electronic states: $\Omega = \Lambda + \Sigma$:

$$|^{2S+1}\Lambda_{\Omega}\rangle = |X^2\Pi_{3/2}\rangle, |X^2\Pi_{1/2}\rangle, |1^2\Sigma_{1/2}\rangle, |1^4\Sigma_{3/2}^-\rangle, |1^4\Sigma_{1/2}^-\rangle, \\ |1^4\Pi_{5/2}\rangle, |1^4\Pi_{3/2}\rangle, |1^4\Pi_{1/2}\rangle, |A^2\Sigma_{1/2}\rangle$$

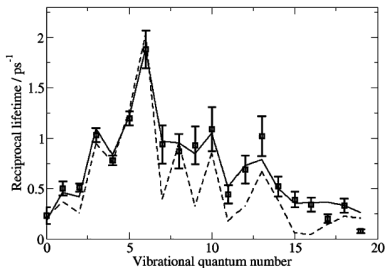
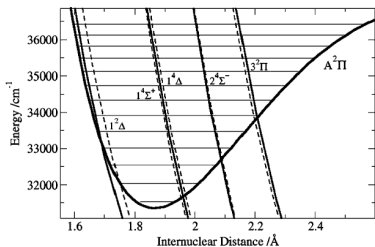
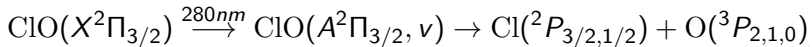
Multichannel expansion: $|\Psi_J\rangle = \sum_{S\Lambda\Omega} |^{2S+1}\Lambda_{\Omega}\rangle |J\Omega M\rangle c_{S\Lambda\Omega J}(R)$

Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hat{J}^2}{2\mu R^2} + H_{\text{BO}} + H_{\text{SO}}$

- Born-Oppenheimer: H_{BO} (5 potentials)
- Spin orbit coupling: H_{SO} : $\Omega \leftrightarrow \Omega$ (9 unique couplings)
- Coriolis coupling \hat{J}^2 : $\Omega \leftrightarrow \Omega \pm 1$ (3 unique couplings)

G. Parlant and D. R. Yarkony, J. Chem. Phys. **110**, 363 (1999)

Predissociation of $\text{ClO}(X^2\Pi_{3/2})$, correlated products



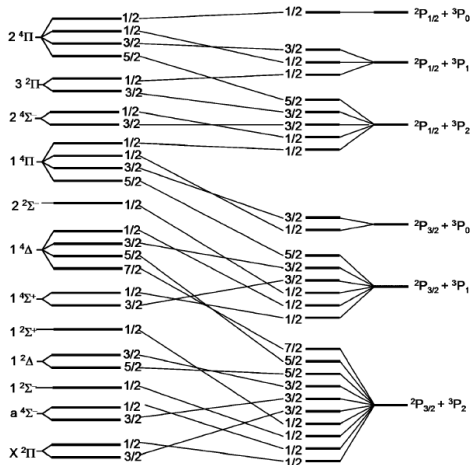
K. Dooley, M. Grubb, J. Geidosh, M. van Beek, G. Groenenboom, and S. North, PCCP **11**, 4770 (2009)

H. Kim, K. Dooley, G. Groenenboom, and S. North, PCCP **8**, 2964 (2006)

I. Lane, W. Howie, A. Orr-Ewing, PCCP **1**, 3087 (1999); PCCP **1**, 3079 (1999)

A. Toniolo, M. Persico, Pitea, J. Chem. Phys. **112**, 2790 (2000)

Predissociation of ClO, adiabatic model



Molecular states:

$$2S+1\Lambda_{\Omega}$$

Atomic states:

$$\text{Cl}(J_{\text{Cl}}, \Omega_{\text{Cl}}) + \text{O}(J_{\text{O}}, \Omega_{\text{O}})$$

Model: correlate

$$\Omega = \Omega_{\text{Cl}} + \Omega_{\text{O}}$$

Expected to work for low kinetic energy

Predissociation of ClO, diabatic model

Atomic fine structure states: $|J_{\text{Cl}}\Omega_{\text{Cl}}\rangle|J_{\text{O}}\Omega_{\text{O}}\rangle$

Russel-Saunders coupling for atoms ($\Omega_i = \Lambda_i + \Sigma_i$):

$$|J_i\Omega_i\rangle = \sum_{\Lambda_i\Sigma_i} |L_i\Lambda_i\rangle|S_i\Sigma_i\rangle\langle L_i\Lambda_i S_i\Sigma_i|J_i\Omega_i\rangle, \quad i = \text{Cl, O}$$

Coupled atomic spin gives molecular spin ($\Sigma = \Sigma_{\text{Cl}} + \Sigma_{\text{O}}$)

$$|S\Sigma\rangle = \sum_{\Sigma_{\text{Cl}}\Sigma_{\text{O}}} |S_{\text{Cl}}\Sigma_{\text{Cl}}\rangle|S_{\text{O}}\Sigma_{\text{O}}\rangle\langle S_{\text{Cl}}\Sigma_{\text{Cl}} S_{\text{O}}\Sigma_{\text{O}}|S\Sigma\rangle$$

Orbital part $\Lambda = \Lambda_{\text{Cl}} + \Lambda_{\text{O}}$:

$$|L\Lambda\rangle = \sum_{\Lambda_{\text{Cl}}\Lambda_{\text{O}}} |L_{\text{Cl}}\Lambda_{\text{Cl}}\rangle|L_{\text{O}}\Lambda_{\text{O}}\rangle\langle L_{\text{Cl}}\Lambda_{\text{Cl}} L_{\text{O}}\Lambda_{\text{O}}|L\Lambda\rangle$$

Fine structure branching in diabatic or sudden limit:

$$P_{J_{\text{Cl}}, J_{\text{O}}}^{(L\Lambda S\Sigma)} = \sum_{\Omega_{\text{Cl}}\Omega_{\text{O}}} |\langle J_{\text{Cl}}\Omega_{\text{Cl}} J_{\text{O}}\Omega_{\text{O}}|L\Lambda S\Sigma\rangle|^2$$
$$= \sum_{\Omega_{\text{Cl}}\Omega_{\text{O}}\Lambda_{\text{Cl}}\Lambda_{\text{O}}\Sigma_{\text{Cl}}\Sigma_{\text{O}}} |\langle L_{\text{Cl}}\Lambda_{\text{Cl}} S_{\text{Cl}}\Sigma_{\text{Cl}}|J_{\text{Cl}}\Omega_{\text{Cl}}\rangle\langle L_{\text{O}}\Lambda_{\text{O}} S_{\text{O}}\Sigma_{\text{O}}|J_{\text{O}}\Omega_{\text{O}}\rangle\langle S_{\text{Cl}}\Sigma_{\text{Cl}} S_{\text{O}}\Sigma_{\text{O}}|S\Sigma\rangle\langle L_{\text{Cl}}\Lambda_{\text{Cl}} L_{\text{O}}\Lambda_{\text{O}}|L\Lambda\rangle|^2$$

Results for ClO fine structure branching

Atomic States	$v' = 0$	$v' = 1$	$v' = 2$	$v' = 3$	$v' = 4$	$v' = 5$	$v' = 6$	$v' = 7$	$v' = 8$	$v' = 9$	$v' = 10$	$v' = 11$
Cl($^2P_{3/2}$) + O(3P_2)	0.10	0.07	0.24	0.26	0.21	0.28	0.19	0.22	0.09	0.29	0.24	0.19
Coupled channel:	0.35	0.34	0.33	0.30	0.28	0.24	0.25	0.32	0.26	0.30	0.26	0.28
Diabatic:	0.17	0.18	0.22	0.23	0.22	0.26	0.27	0.22	0.24	0.22	0.25	0.17
Cl($^2P_{1/2}$) + O(3P_2)	0.37	0.31	0.37	0.09	0.12	0.08	0.18	0.02	0.10	0.18	0.26	0.31
Coupled channel:	0.20	0.18	0.20	0.18	0.19	0.14	0.13	0.22	0.12	0.23	0.11	0.12
Diabatic:	0.21	0.20	0.19	0.22	0.20	0.25	0.28	0.20	0.22	0.19	0.23	0.13
Cl($^2P_{3/2}$) + O(3P_1)	0.37	0.56	0.29	0.41	0.35	0.22	0.15	0.19	0.24	0.17	0.21	0.37
Coupled channel:	0.37	0.39	0.31	0.32	0.30	0.28	0.28	0.31	0.28	0.32	0.30	0.30
Diabatic:	0.29	0.30	0.34	0.31	0.33	0.29	0.28	0.33	0.31	0.33	0.31	0.37
Cl($^2P_{1/2}$) + O(3P_1)	0.10	0.00	0.07	0.00	0.00	0.16	0.22	0.34	0.21	0.30	0.16	0.00
Coupled channel:	0.02	0.03	0.02	0.02	0.06	0.11	0.11	0.04	0.11	0.04	0.09	0.09
Diabatic:	0.21	0.19	0.09	0.10	0.09	0.07	0.07	0.10	0.08	0.09	0.08	0.12
Cl($^2P_{3/2}$) + O(3P_0)	0.06	0.06	0.04	0.24	0.33	0.26	0.26	0.22	0.32	0.06	0.13	0.13
Coupled channel:	0.06	0.07	0.13	0.17	0.17	0.24	0.24	0.12	0.24	0.11	0.24	0.21
Diabatic:	0.12	0.13	0.17	0.14	0.16	0.13	0.11	0.16	0.15	0.17	0.14	0.20
Cl($^2P_{1/2}$) + O(3P_0)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.00	0.00
Coupled channel:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Diabatic:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4772 | *Phys. Chem. Chem. Phys.*, 2009, 11, 4770–4776

This journal is © the Owner Societies 2009

Coupled channel, Fermi golden rule:

$$\Gamma_{v'; J_{Cl} J_O}^{(n)} = \frac{2\pi}{\hbar} |\langle A^2 \Pi_{3/2}(v') | \hat{H}_{A,n} | \Psi_{J_{Cl} \Omega_{Cl} J_O \Omega_O} \rangle|^2.$$

Results for ClO fine structure branching

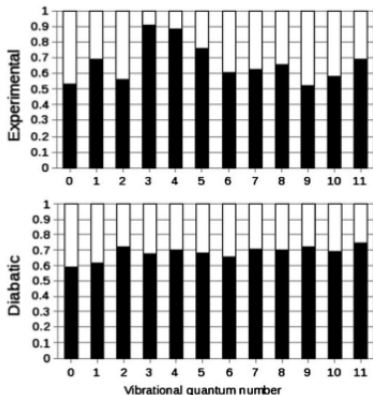


Fig. 4 Overall Cl(²P_{3/2}) (dark) and Cl(²P_{1/2}) (white) branching ratios as a function of $A^2\Pi_{3/2}$ vibrational level. The results from experiment and the diabatic limit model, are shown in the top and bottom panels respectively.

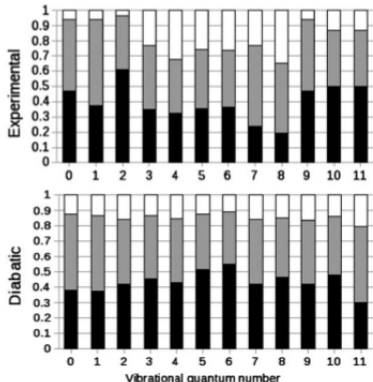


Fig. 5 Overall O(³P₂) (black), O(³P₁) (grey), and O(³P₀) (white) populations for each as a function of $A^2\Pi_{3/2}$ vibrational level. The results from experiment and the diabatic limit model are shown in the top and bottom panels respectively.

Results for ClO fine structure branching

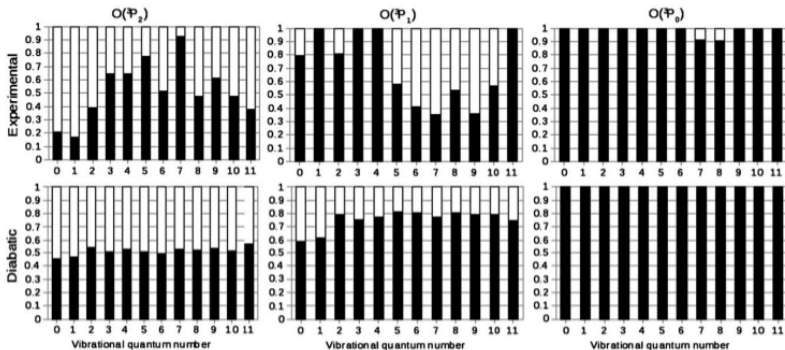
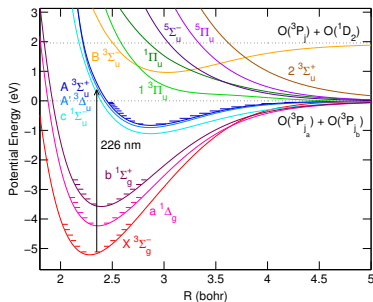
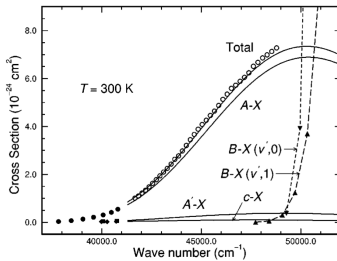


Fig. 6 $Cl(^2P_{3/2})$ and $Cl(^2P_{1/2})$ branching ratios for each oxygen fine-structure state as a function of $A^2\Pi_{3/2}$ vibrational level. The results from experiment and the diatomic limit model are shown in the top and bottom panels respectively.

Forbidden transitions: oxygen Herzberg I, II, and III



J. Chem. Phys., Vol. 108, No. 17, 1 May 1998

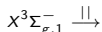


- Herzberg I: $A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$
- Herzberg II: $c^1\Sigma_u^- \leftarrow X^3\Sigma_g^-$
- Herzberg III: $A'^3\Delta_u \leftarrow X^3\Sigma_g^-$

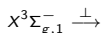
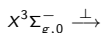
B. Buisse, W. van der Zande, A. Eppink, D. Parker, B. Lewis, and S. Gibson, J. Chem. Phys. **108**, 7229 (1998)

Pathways for Herzberg I transition

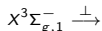
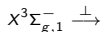
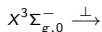
- Spin-orbit through ${}^3\Sigma_u^-$ (2 states)



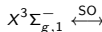
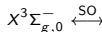
- Spin-orbit through ${}^3\Pi_u$, (3 states)



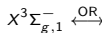
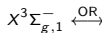
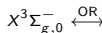
- Orbit-rotation through ${}^3\Pi_u$, (3 states)



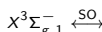
- Spin-orbit through ${}^3\Pi_g$, (2 states)



- Orbit-rotation through ${}^3\Pi_g$, (2 states)

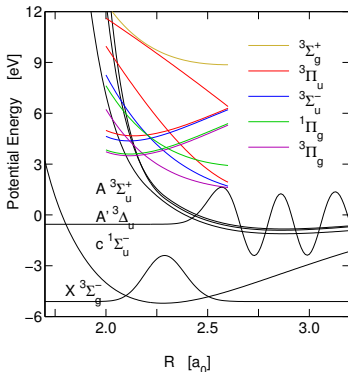
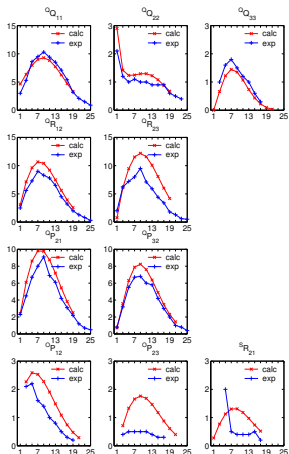


- Spin-orbit through ${}^3\Sigma_g^+$ (1 state)



Integrated line cross section for O₂ Herzberg I

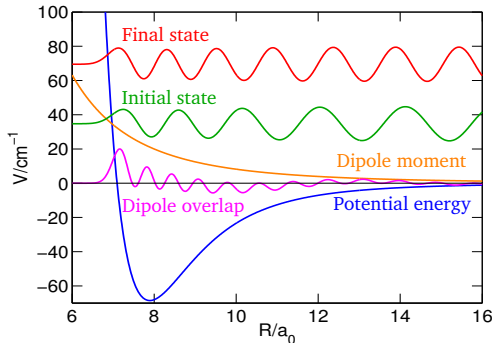
Cross-sections in 10^{-26} cm² molecule⁻¹ cm⁻¹



Experiment: M.-F. Mérienne *et al.*, J. Mol. Spectrosc. **202**, 171 (2000).

Theory: PhD thesis Mirjam van Vroonhoven, Nijmegen, 2003

Collision induced absorption (CIA)



- $\text{H}_2(N)+\text{H}_2(N')$, **Tijs Karman**, A. van der Avoird, G. Groenenboom, J. Chem. Phys. (2015), accepted
- $\text{N}_2(N)+\text{N}_2(N')$, **Tijs Karman**, E. Milliordos, K. Hunt, G. Groenenboom, A. van der Avoird, J. Chem. Phys. (2015), accepted

CIA absorption coefficient **quadratic** in monomer density
Dominant contribution from continuum states (integral sign)

$$\alpha(\omega, T) = \frac{2\pi^2}{3\hbar c} n^2 \omega \left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right) \right] V g(\omega, T)$$

Spectral density:

$$g(\omega, T) = \int_i \int_f P^{(i)}(T) |\langle i | \hat{\mu} | f \rangle|^2 \delta(\omega_f - \omega_i - \omega).$$

Multichannel expansion of wave function

Coupled angular basis function

$$|(N_A N_B) N_L; JM\rangle = \sum_{M_A, M_B, M_N, M_L} |N_A M_A\rangle |N_B M_B\rangle |L M_L\rangle \\ \times \langle N_A M_A N_B M_B | N M_N \rangle \langle N M_N L M_L | J M \rangle$$

Expansion of the potential in coupled spherical harmonics

$$V(R) = \sum_{l_1, l_2, l} V_{l_1, l_2, l}(R) \left[\left[C^{(l_1)}(\hat{r}_A) \otimes C^{(l_2)}(\hat{r}_B) \right]^{(l)} \otimes C^{(l)}(\hat{R}) \right]_0^{(0)}$$

Expansion of spherical components of the dipole moment

$$\mu_{\nu}(R) = \sum_{l_1, l_2, l, \lambda} D_{l_1, l_2, l, \lambda}(R) \left[\left[C^{(l_1)}(\hat{r}_A) \otimes C^{(l_2)}(\hat{r}_B) \right]^{(l)} \otimes C^{(\lambda)}(\hat{R}) \right]_{\nu}^{(1)}$$

Isotropic interaction approximation: separation of degrees of freedom. (Keep angular dependence of dipole surfaces)

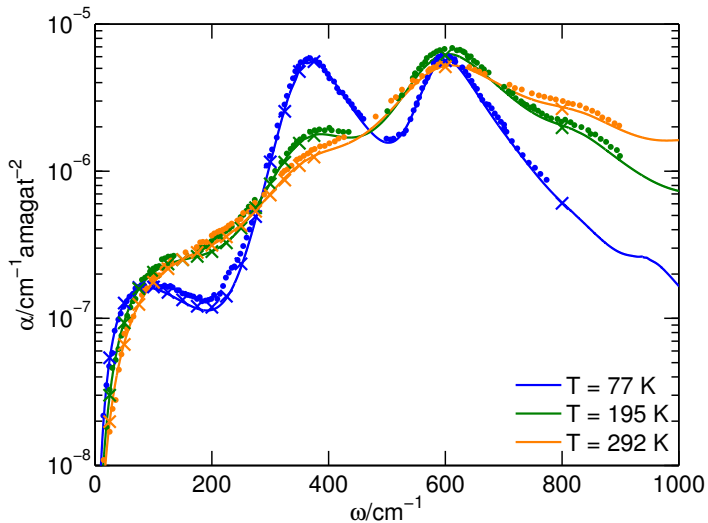
$$|(N_A N_B)NL; JME_{\text{col}}\rangle = |(N_A N_B)NL; JM\rangle|E_{\text{col}}, L\rangle,$$
$$\langle R|E_{\text{col}}, L\rangle = \frac{1}{R} U_{E_{\text{col}}, L}(R).$$

Coupled-states approximation: neglect off-diagonal coriolis coupling.

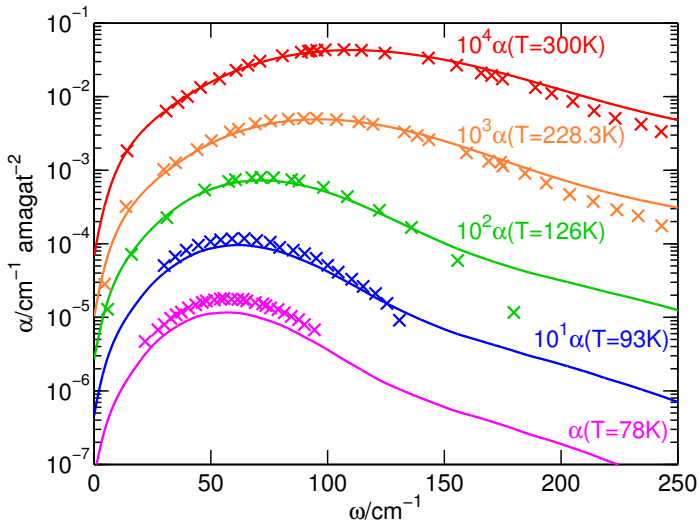
$$\hat{L}^2 = (\hat{\mathbf{J}} - \hat{\mathbf{N}})^2 \approx \hat{J}^2 + \hat{N}^2 - 2\hat{J}_z \hat{N}_z$$

Coupled channels: Numerically exact calculation of the dipole coupling.

Usual isotropic interaction accurate for H_2 .

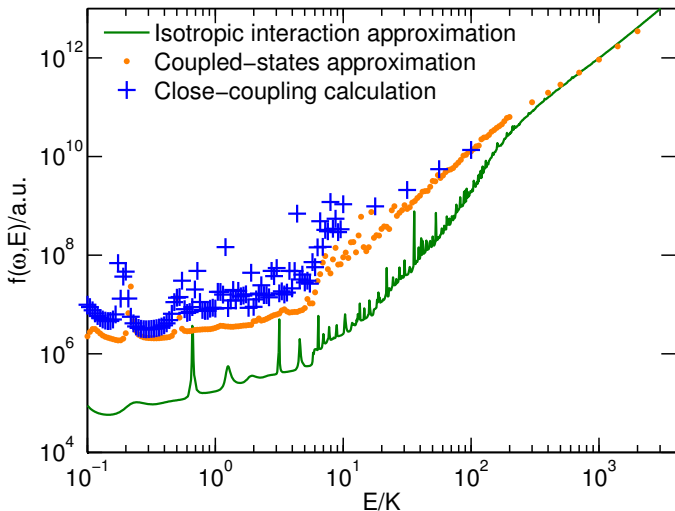


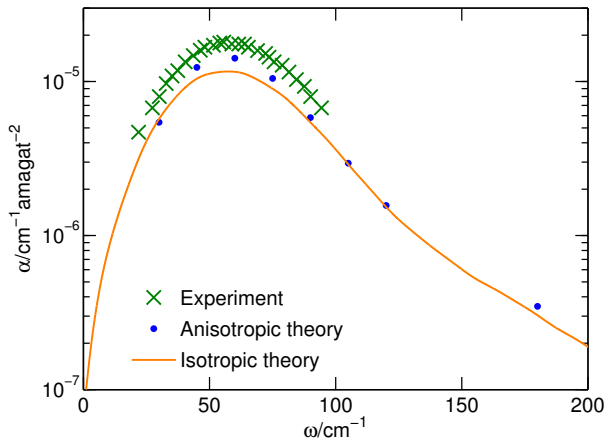
Isotropic interaction approximation for high T.



Large effects of anisotropy for low energy.

Coupled-states approximation captures effect of anisotropy.

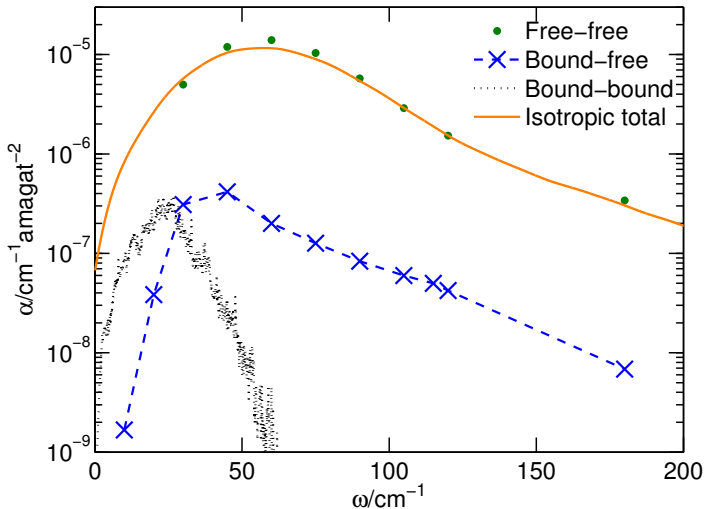




Anisotropic calculations improve agreement with experiment (19 %).

Bound-free contribution about 1 % at $T = 78$ K.

Contribution about 10 % at $T = 50$ K.



- Photodissociation finestructure branching ratios
- Predissociation rates
- Forbidden transitions
- Collision induced absorption

Question: what is most urgently needed in astrochemistry?



Theory Nijmegen

- Mirjam van Vroonhoven (O_2)
- Mark van der Loo (OH, H_2)
- Marloes van Beek (ClO)
- Liesbeth Janssen (OH, SH)
- Tijs Karman (CIA)
- Prof. Ad van der Avoird (CIA)

Funding: NWO

