



An Analysis of the Vibronic Spectrum of Chlorine Dioxide



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Background

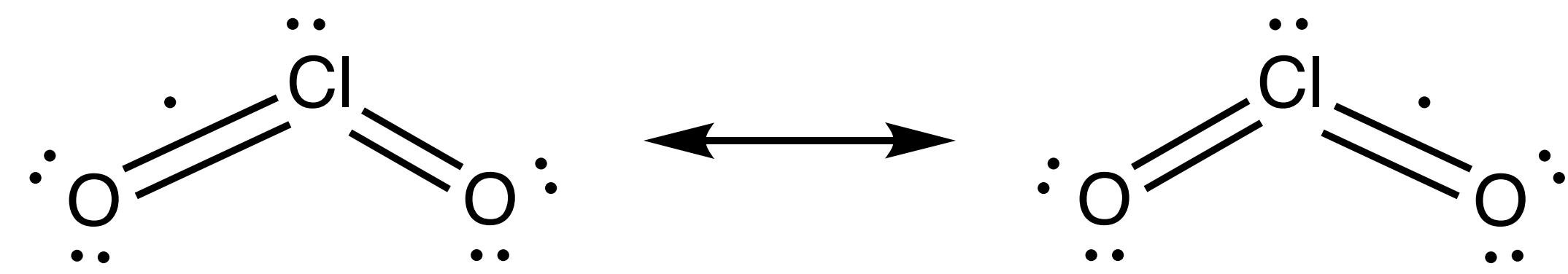


Figure 1. Electronic structure of chlorine dioxide described by its resonance structures for a three electron bond.

- Chlorine dioxide (ClO₂) is an uncharged free radical with C_{2v} symmetry
- The best proposed electronic structure was by Brockway and Pauling, with a double bond on one side and a single and three electron bond on the other side^{1,2}
- Experimentally measured bent geometry with a bond angle of 117.6° with a dipole moment of 1.792 D
- Exists as a yellow gas at STP, reddish-brown liquid at 11 °C and orange-brown solid at -59 °C
- Gaseous ClO₂ is highly soluble in water over a wide pH range
- ClO₂ has 3 fundamental vibrational modes
- Since the 1920's the absorption spectrum for ClO₂ was found to have distinct peaks and not just a single absorption peak³
- The structure is a product of the coupling between the electronic excitation and the vibrational energies creating a vibronic spectrum

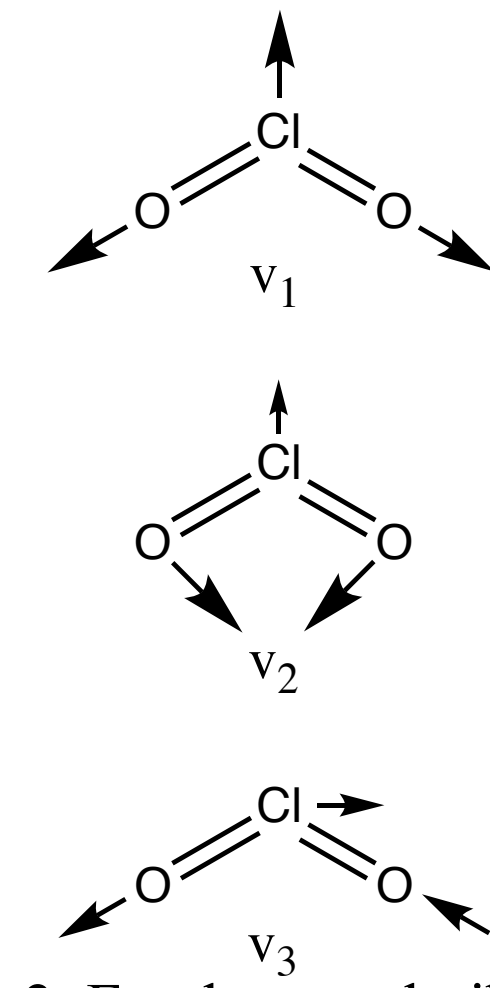


Figure 2. Fundamental vibrational modes of ClO₂ with C_{2v} symmetry

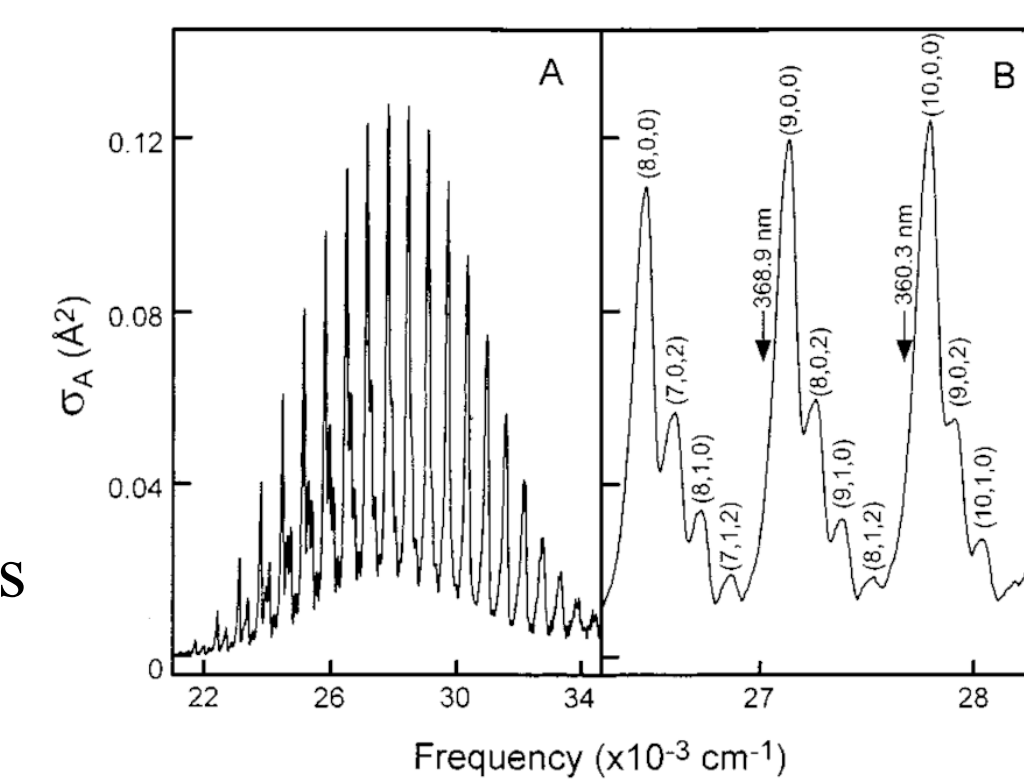


Figure 3. Previously observed vibronic spectrum for ClO₂ (4).

Theory

- The wave function of the molecule can be described in terms of the nuclear and electronic wave functions. The Born-Oppenheimer approximation states that the wave function of the electron is uncoupled from the wave function of the nuclei

$$|\Psi\rangle = |\psi_e \psi_n\rangle \quad (1)$$

- The ψ_n is defined by the rotational and vibrational wave functions but we neglect the rotational levels

$$|\psi_n\rangle = |\psi_{rot} \psi_v\rangle = |\psi_v\rangle \quad (2)$$

- The transition dipole moment operator, μ , is used to determine the strength of the interaction with light that led to a transition from ψ^i to ψ^f

$$\langle \psi_e^i \psi_v^i | \mu | \psi_e^f \psi_v^f \rangle = \langle \psi_e^i \psi_v^i | \mu_e + \mu_n | \psi_e^f \psi_v^f \rangle \quad (3)$$

- Since μ_n leaves ψ_e unchanged and ψ_e^i and ψ_e^f are orthogonal states

$$\langle \psi_e^i \psi_v^i | \mu_e | \psi_e^f \psi_v^f \rangle + \langle \psi_e^i \psi_v^i | \mu_n | \psi_e^f \psi_v^f \rangle = \langle \psi_e^i \psi_v^i | \mu_e | \psi_e^f \psi_v^f \rangle \quad (4)$$

- This means that the probability amplitude, or intensity is given by

$$P = \langle \psi_v^i | \psi_v^f \rangle \langle \psi_e^i | \mu_e | \psi_e^f \rangle \quad (5)$$

Where $\langle \psi_v^i | \psi_v^f \rangle$ is known as the Franck-Condon Factor describing the vibrational overlap integral from the ground to an excited state.

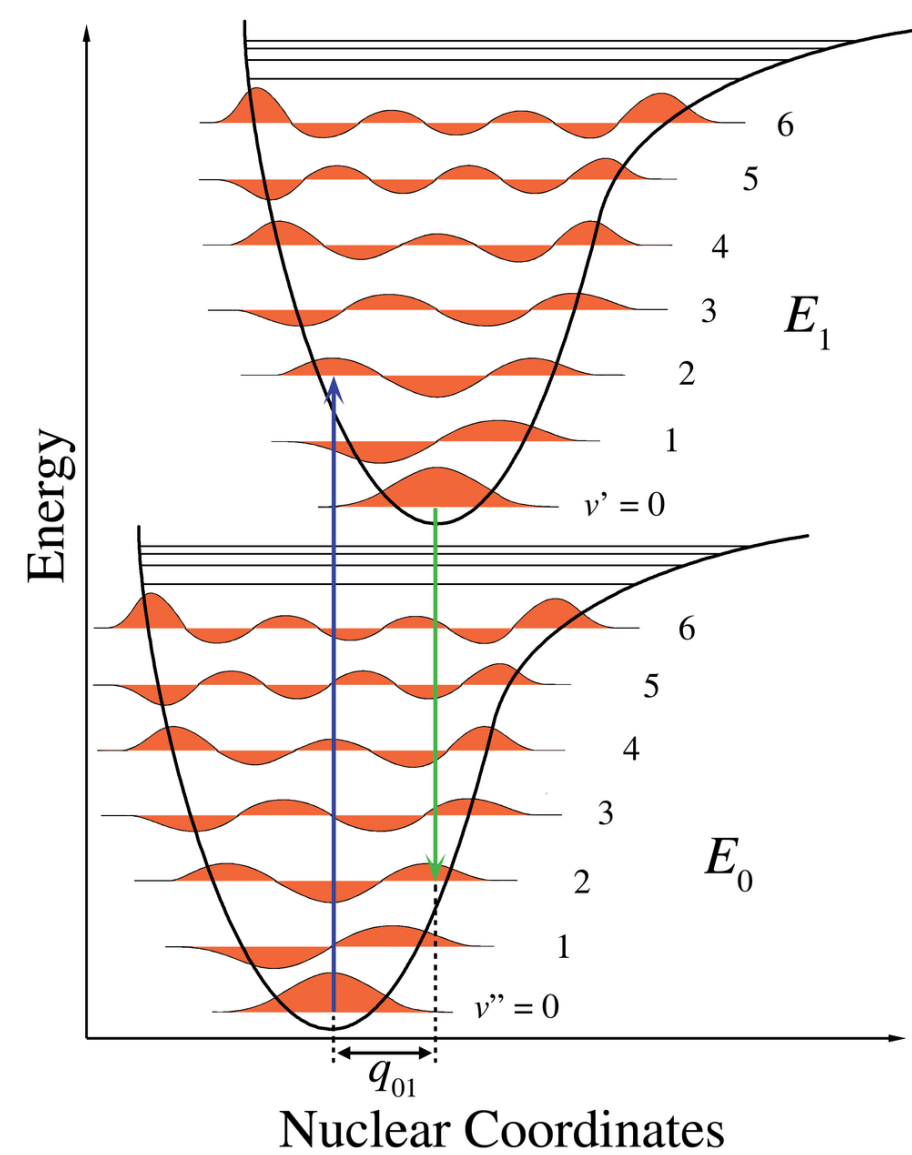


Figure 4. Visual description of absorption and vibration coupling leading to Franck-Condon Factors⁵.

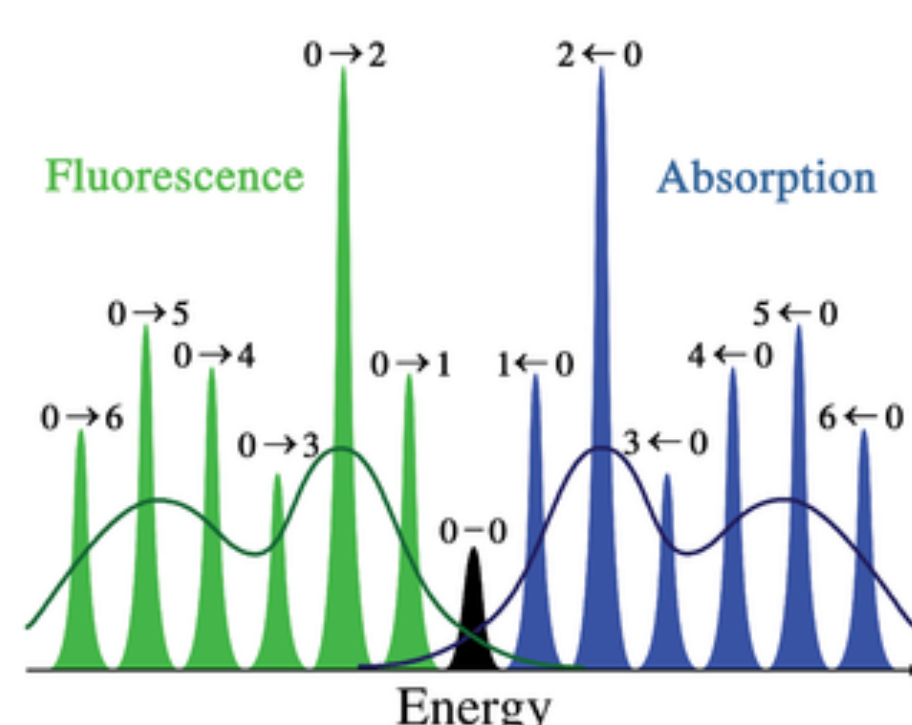
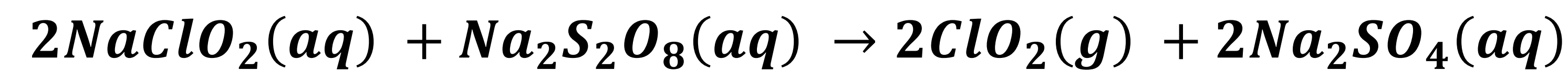


Figure 5. A visual description of the effect that vibronic coupling has on an absorption spectrum⁵.

Methods



Synthesis

- Dissolved 1.58 g of Na₂S₂O₈ in 50 mL of H₂O
- Dissolved 1.79 g of NaClO₂ in 50 mL of H₂O
- Drip the Na₂S₂O₈ solution into the NaClO₂ solution at 80 drips per minute
- The ClO₂ gas that is generated is bubbled out of the flask by N₂ and through a glass tube with Ascarite to remove Cl₂ gas
- The gas is then flowed into 50 mL of H₂O
- Gas was collected for 1 hour
- A UV-Vis was collected after extracting the ClO₂ gas into diethyl ether

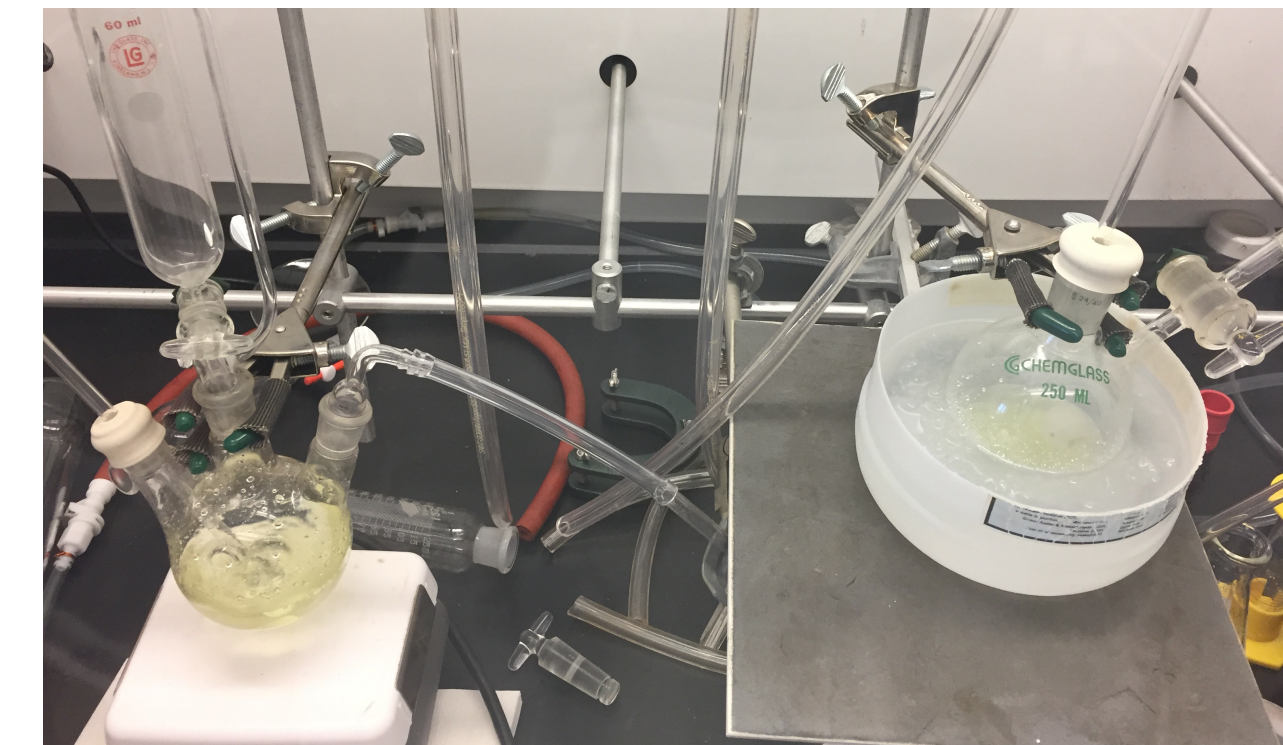


Figure 6. A successful synthesis produces a distinct yellow-green in both the reaction flask (left) and the collection flask (right)

Computation

- Constructed ClO₂ using GAUSSIAN 09W
- Optimization and frequency calculation of ground state with MP2/aug-cc-pVTZ⁶
- Optimization and frequency calculations of first excited state with CIS/aug-cc-pVTZ
- Use to calculate the energy for the transition from ground state to first excited state as well as the vibrational frequencies of the symmetric stretch modes

Vibronic Spectrum

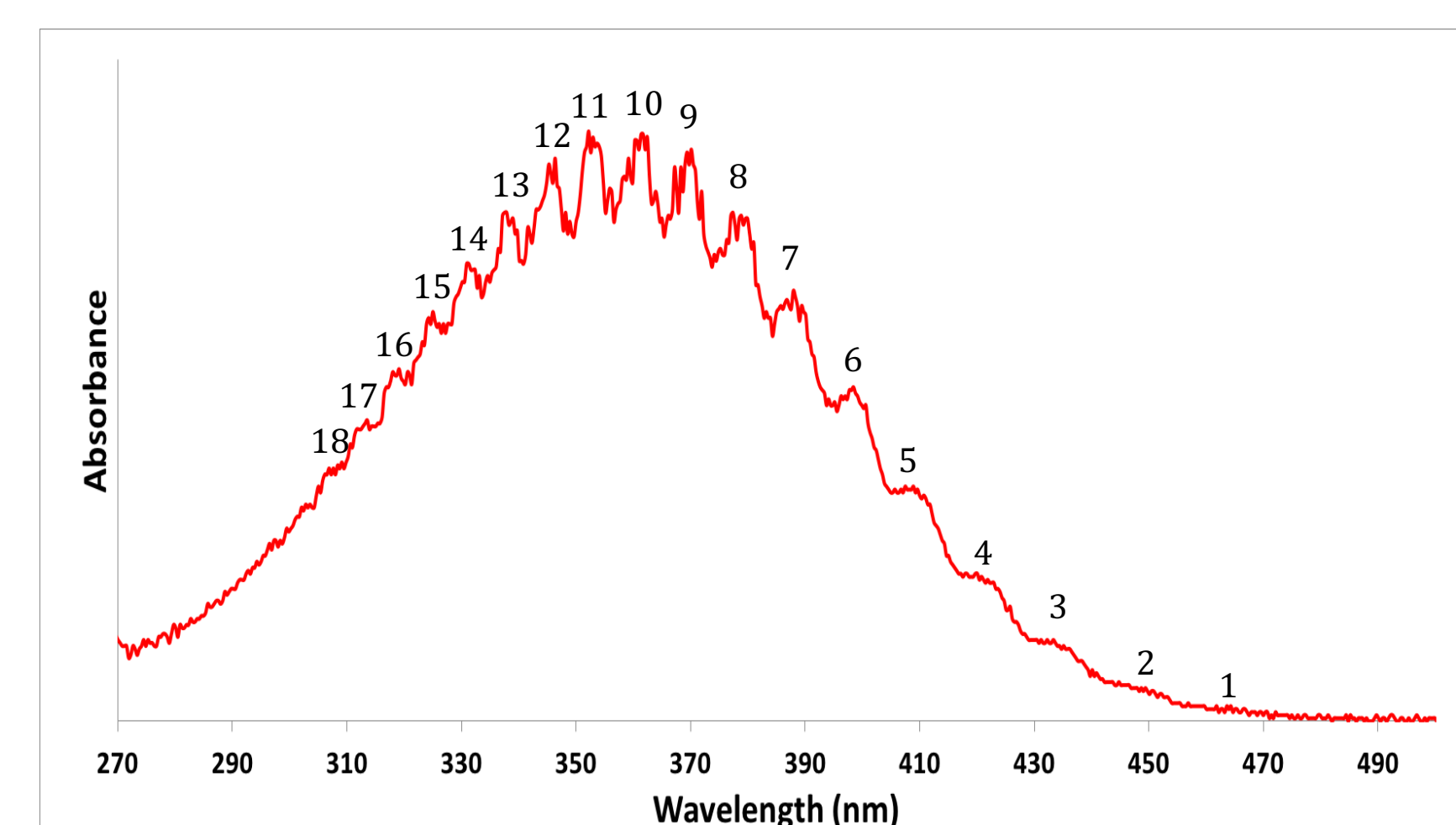


Figure 7. Experimentally measured UV-Vis vibronic spectrum for ClO₂ in diethyl ether at room temperature.

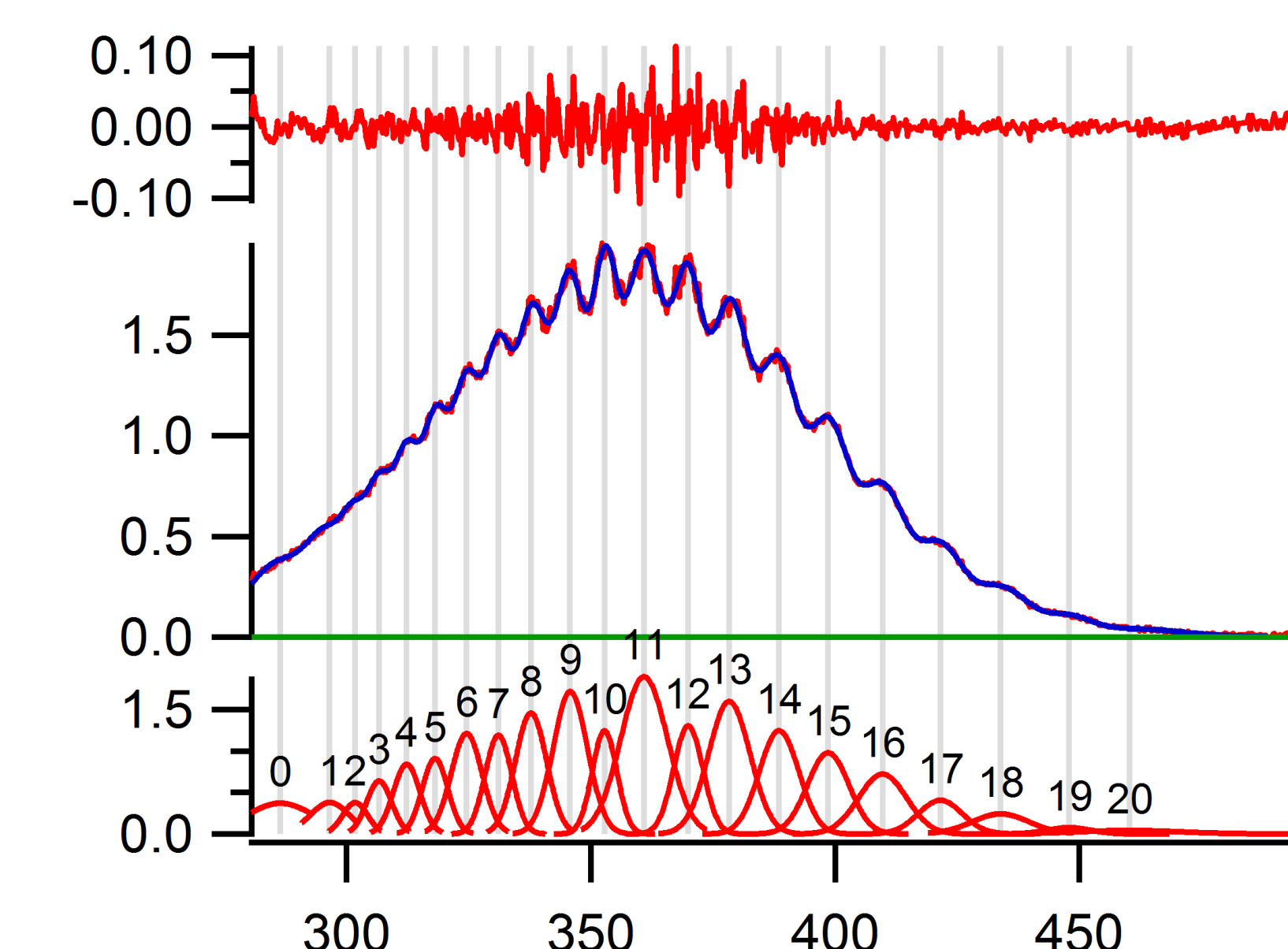


Figure 8. Results of a multipeak fitting performed on the vibronic spectrum in Figure 7. The labels in the plot on the bottom do not match those in Figure 7. The fitting was performed using IGOR Pro.

Table 1. Peak position obtained from the multipeak fitting in Figure 8. The values from previous measurement come from (Richard & Vaida, 1991)⁴.

Peak #	Mode (v ₁ v ₂ v ₃)	Obs. λ (nm)	Previous λ (nm)
-	(0 0 0)	-	475.8
1	(1 0 0)	460.2	460.3
2	(2 0 0)	447.9	446.0
3	(3 0 0)	433.8	432.6
4	(4 0 0)	421.5	420.1
5	(5 0 0)	409.7	408.4
6	(6 0 0)	398.5	397.4
7	(7 0 0)	388.5	387.1
8	(8 0 0)	378.3	377.4
9	(9 0 0)	369.9	368.2
10	(10 0 0)	360.8	359.6
11	(11 0 0)	352.8	351.4
12	(12 0 0)	345.7	343.6
13	(13 0 0)	337.7	336.3
14	(14 0 0)	331	
15	(15 0 0)	324.5	
16	(16 0 0)	318.1	
17	(17 0 0)	312.3	
18	(18 0 0)	306.6	
19	(19 0 0)	301.7	

Results

1. Calculation of harmonic and anharmonic constants

- The vibrational energy levels can be described by Morse potential with Energy Eigenvalues

$$G_i = E_{00'} + \left(v_i + \frac{1}{2}\right)\omega_0 - \left(v_i + \frac{1}{2}\right)^2 \omega_0 x_e$$

- $E_{00'}$ is the excitation energy from g.s. to e.s., $v_i = 0, 1, 2, \dots$, ω_0 is the fundamental vibration frequency for the symmetric stretch and x_e is the anharmonicity constant, which is used to calculate the Dissociation Energy, D_e

$$x_e = \frac{\omega_0}{4D_e}$$

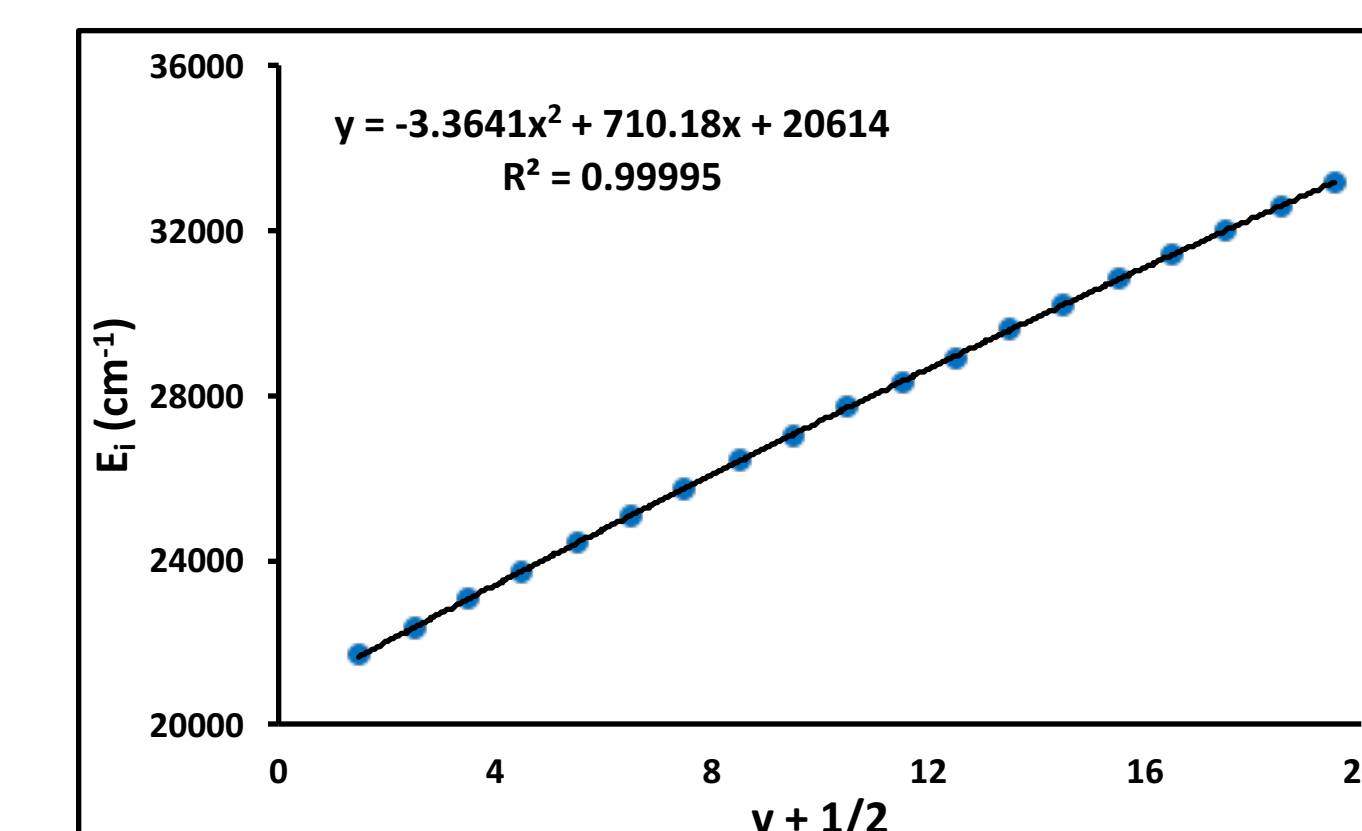


Figure 9. Plot of vibronic peak energies as a function of $v+1/2$ and fit to a 2nd order polynomial.

Table 2. Calculated harmonic and anharmonic constants from the 2nd order fitting function.

Variable	Calculated	cc-pVTZ	Previous ⁴
$E_{00'}$ (cm ⁻¹)	20614	21141	21017.2
ω_0 (cm ⁻¹)	710.18	683	705.9
x_e	0.0047		0.0039
D_e (cm ⁻¹)	37775		45250

2. Birge-Sponer Plot

- Use the vibrational energy levels to calculate the dissociation energy, D_0

$$D_0 = \sum_{v=0}^{v_{max}} \Delta G_{v+1/2}$$

$$\Delta G_{v+1/2} = G(v+1) - G(v)$$

- v_{max} is the maximum vibrational mode where dissociation occurs determined from a linear fit and extrapolating to $\Delta G_{v+1/2} = 0$.

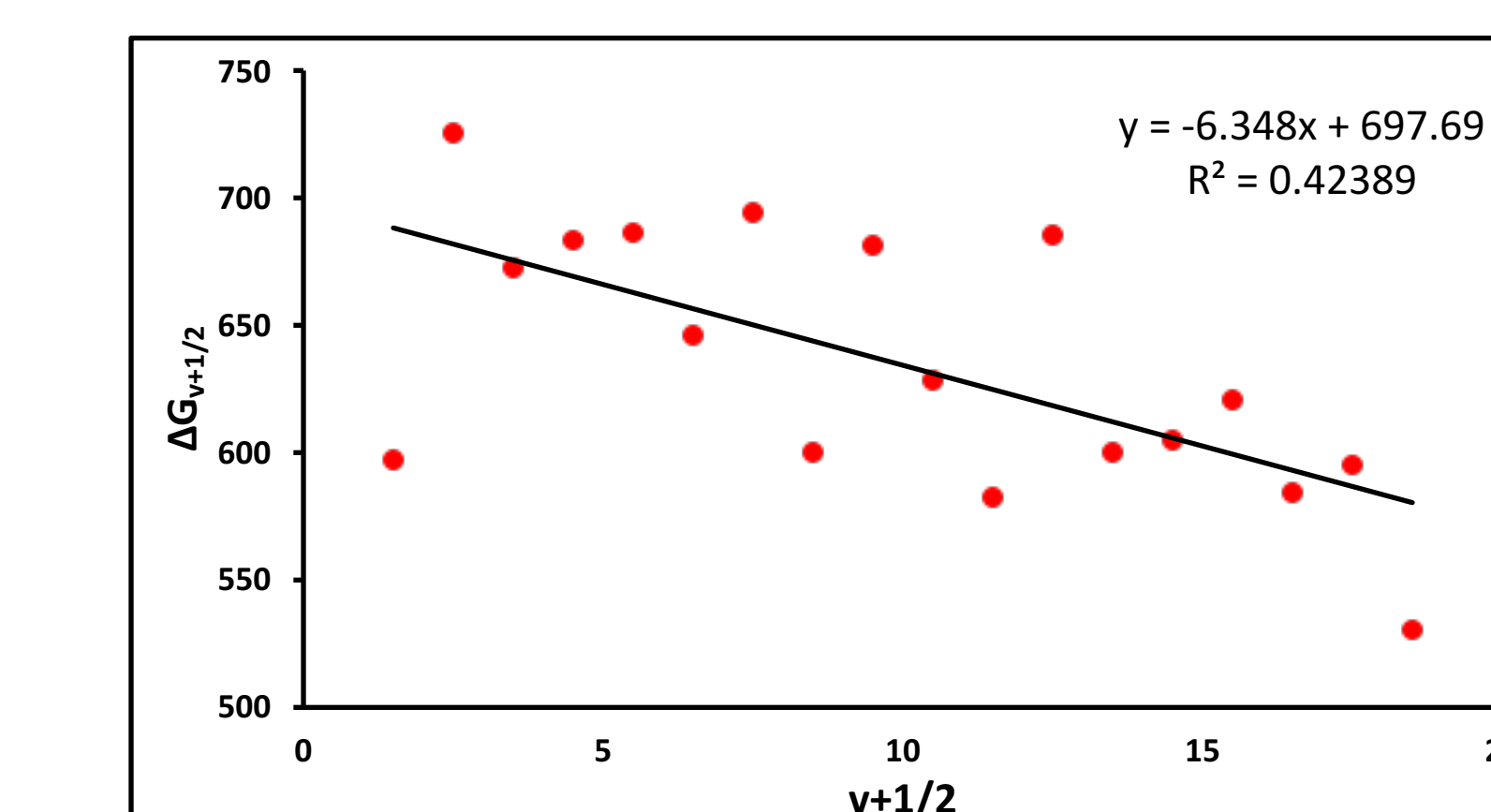


Figure 10. Birge-Sponer plot to calculate the dissociation energy.

Table 3. Values calculated from the fit in Figure 10.

Variable	Value
v_{max}	110
D_0 (cm ⁻¹)	38338

Discussion

- The vibronic spectrum peaks matched previous measurements, but due to the resolution of the spectrometer, I was only able to resolve the symmetric stretches
- The calculation and computation of the harmonic and anharmonic constants agreed well
- The calculated D_0 should be smaller than D_e , most likely the error comes from the poor fitting and typically $\Delta G_{v+1/2}$ drops off before the linear extrapolation to v_{max}

Acknowledgements

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References

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