Can a Simple Hamiltonian Teach Us Anything About NO_3 ?

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The Absorption Coefficient of Nitrogen Pentoxide in the Ultraviolet and the Visible Absorption Spectrum of NO_3

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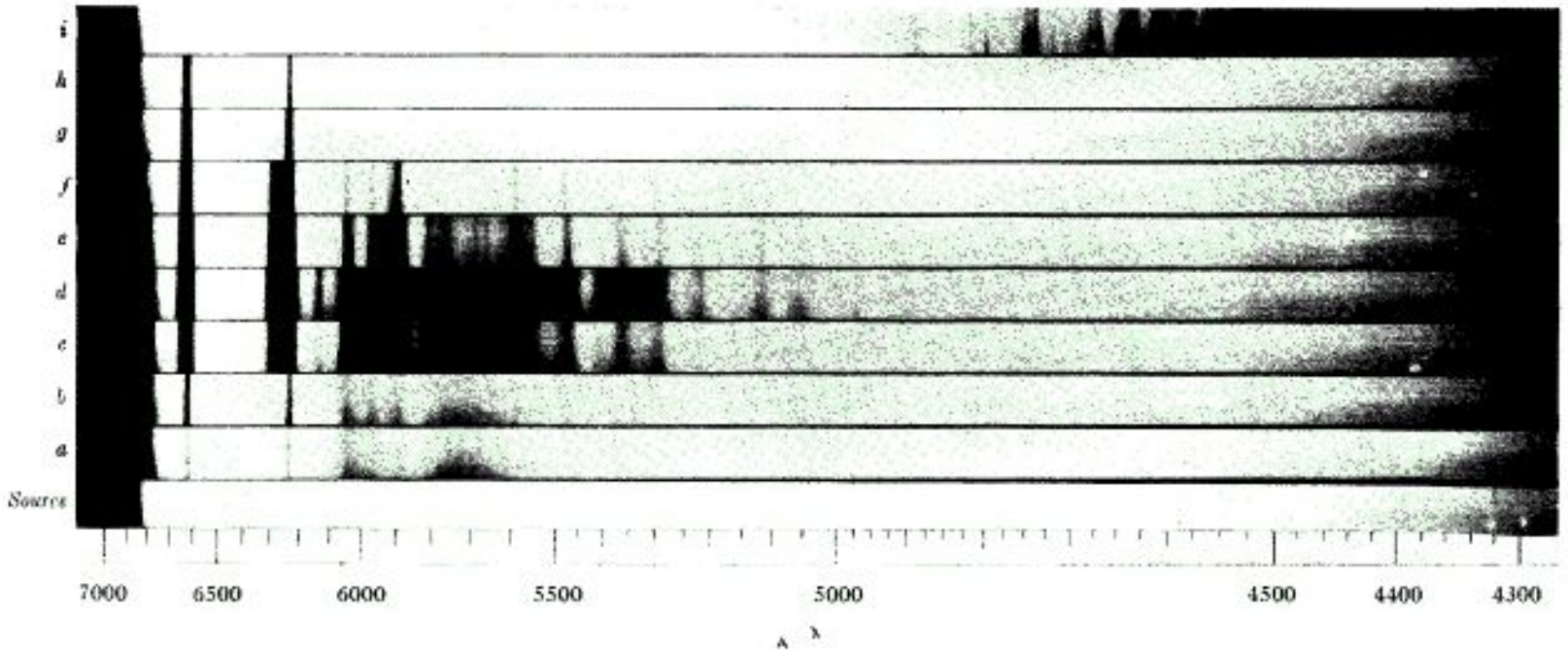
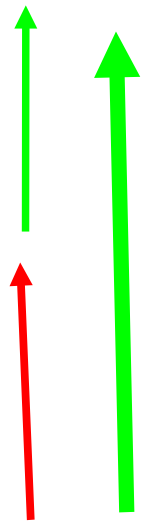
(Received August 9, 1937)



NO_3 Primer

State	Energy	MO configuration
$\tilde{B}^2E'$	15105 cm^{-1}	$\cdots(4e')^1(1e'')^2(1a_2')^1$
$\tilde{A}^2E''$	7064 cm^{-1}	$\cdots(4e')^2(1e'')^1(1a_2')^1$
$\tilde{X}^2A_2'$	0 cm^{-1}	$\cdots(4e')^2(1e'')^2(1a_2')^1$



Vibrational modes

$$\nu_1(a_1{}') \implies \text{Symmetric stretch}$$
$$\nu_2(a_2{}'') \implies \text{Umbrella}$$
$$\nu_3(e') \implies \text{Degenerate stretch}$$
$$\nu_4(e') \implies \text{Degenerate bend}$$

Fundamental Levels of NO_3

Fundamental	Experiment	EOMIP-CCSD
v1	1053 (DF)	1135 (1041)
v2	763 (FTIR)	816 (790)
v3	1492 (DF,FTIR)	1116 (980)
v4	ca. 360 (DF,PES)	266 (411)

Significant disagreement between theory and experiment for v4 and, especially, v3. Experimental position of v3 somewhat at odds with generally accepted pseudo-JT interactions between $\tilde{X}$ and $\tilde{B}$ states.

Hamiltonian

	A_2'	E_a''	E_b''	E_a'	E_b'
A_2'		Quadratic PJT coupling (e' a_2'')		Linear PJT coupling (e')	
E_a''				Linear PJT coupling (a_2'')	
E_b''					
E_a'					
E_b'					

Temperature Dependence of the NO_3 Absorption Spectrum

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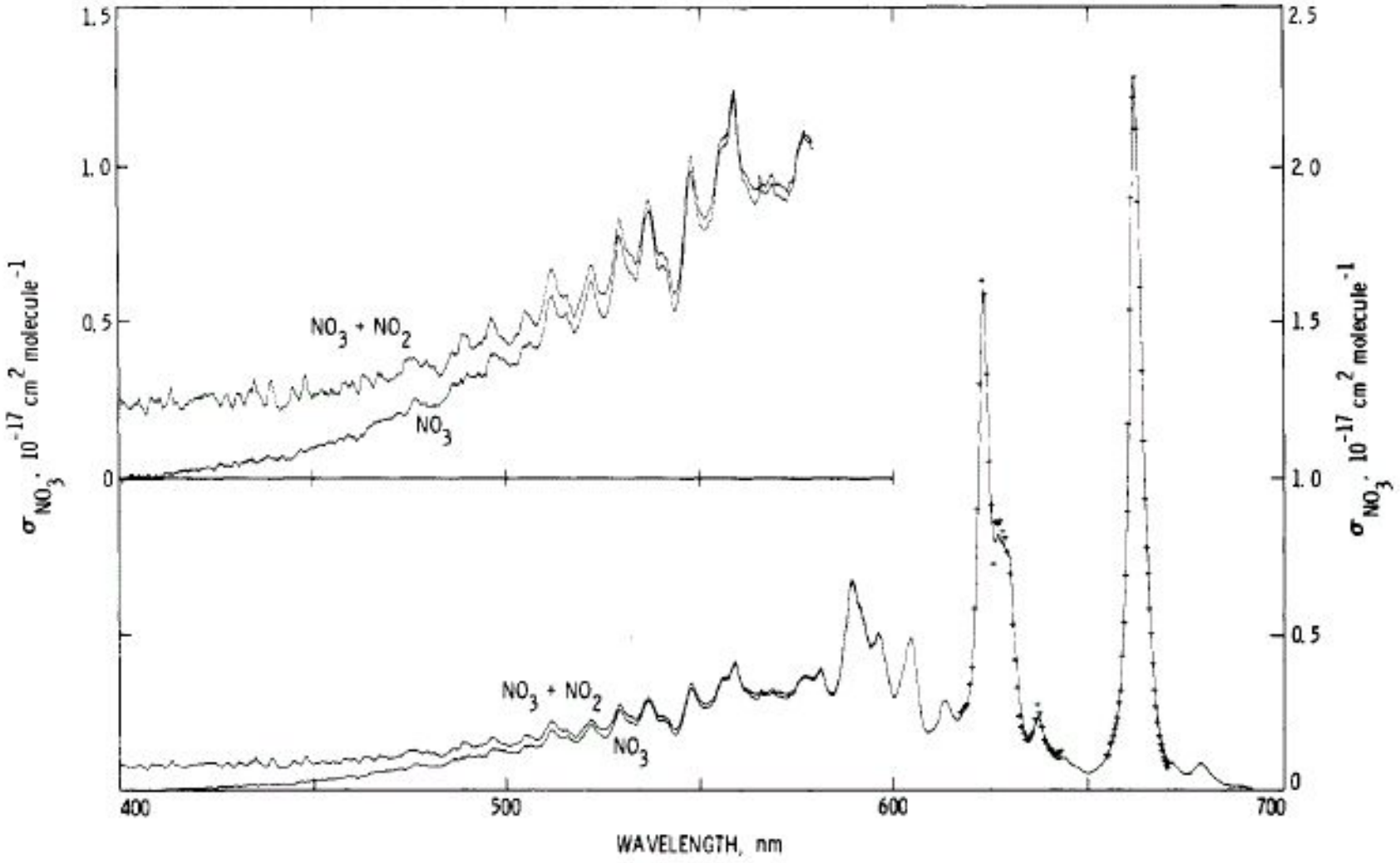
(Received: December 11, 1985; In Final Form: February 13, 1986)



NO_3 radical studied by laser-induced fluorescence

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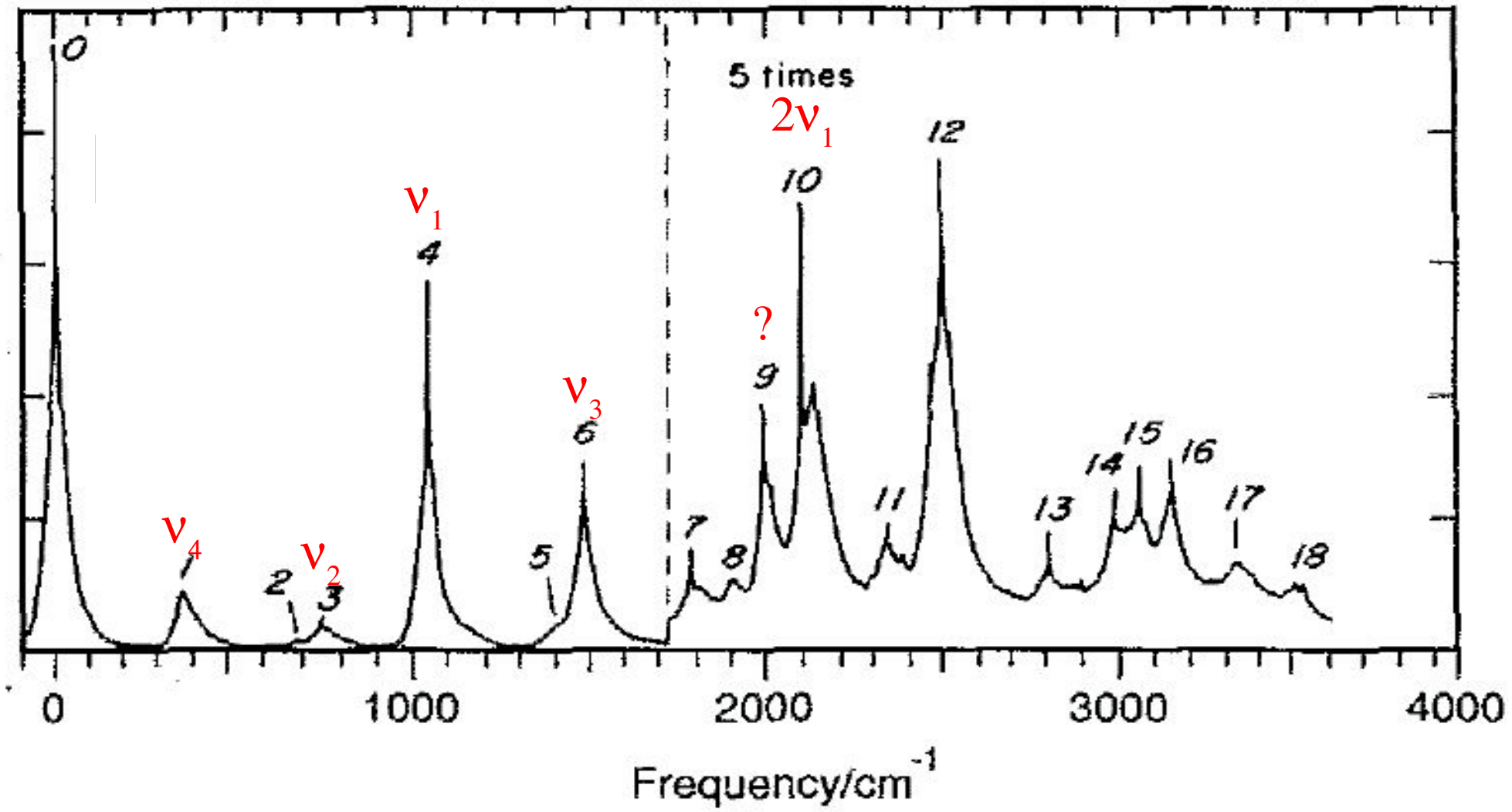
(Received 11 June 1991; accepted 28 October 1991)



Cavity ringdown spectrum of the forbidden $\tilde{A}^2E'' \leftarrow \tilde{X}^2A_2'$ transition of NO_3: Evidence for static Jahn–Teller distortion in the $\tilde{A}$ state

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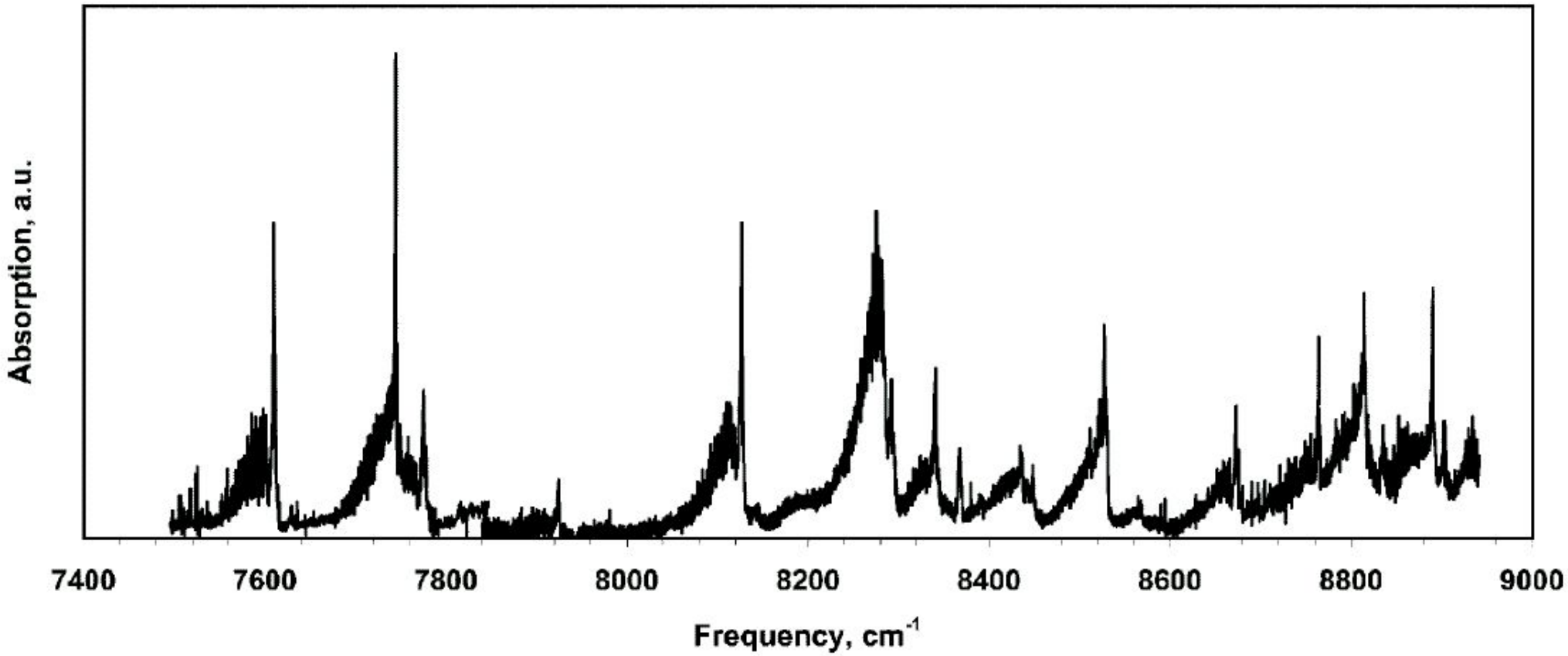
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 10 January 2005; accepted 3 March 2005; published online 13 June 2005)



$\tilde{A} \leftarrow \tilde{X}$ intensity arises partly from $\tilde{X}/\tilde{B}$ mixing! (Stanton & Okumura, unpublished)

Examination of the $^2A_2'$ and $^2E''$ states of NO_3 by ultraviolet photoelectron spectroscopy of NO_3^-

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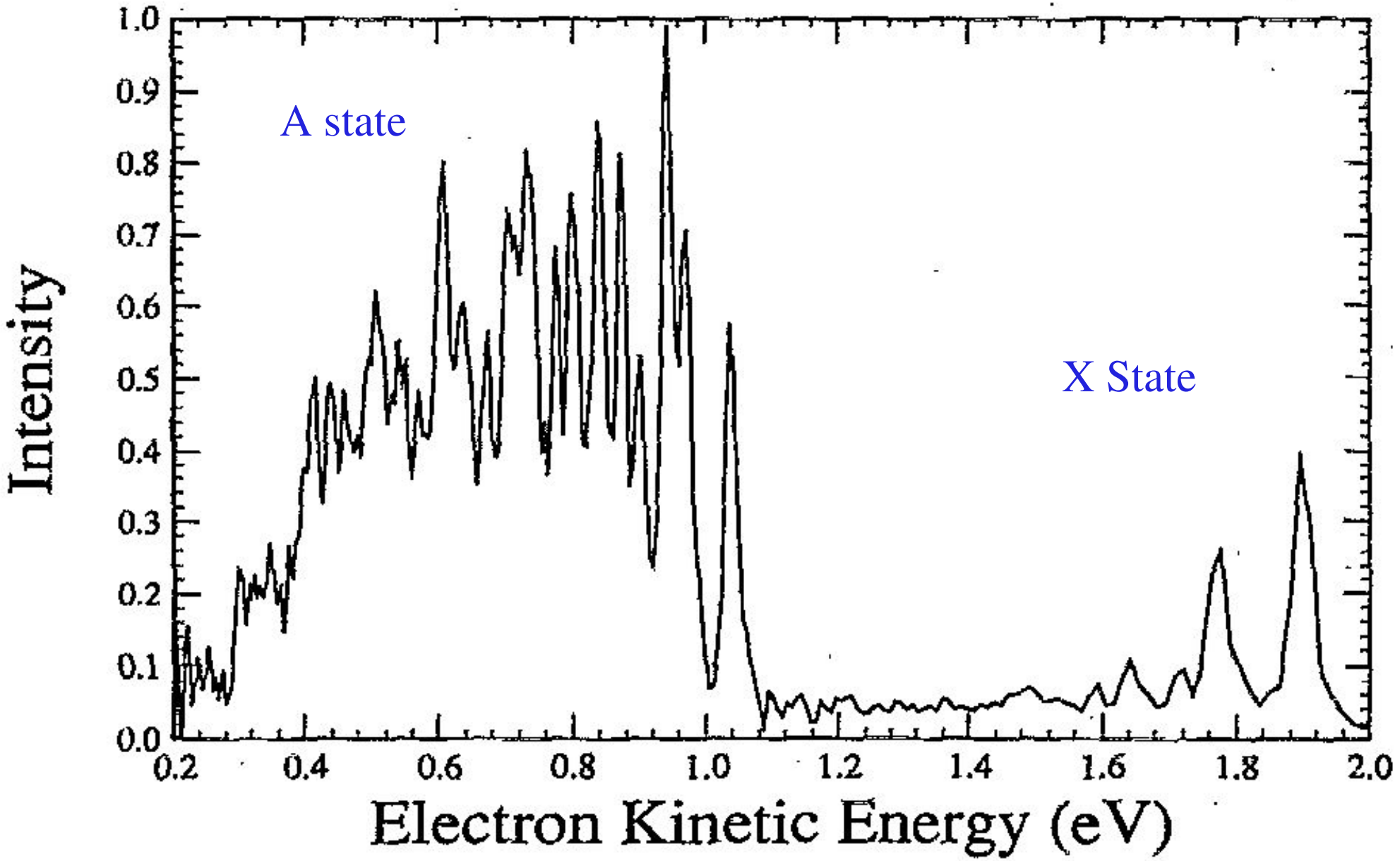
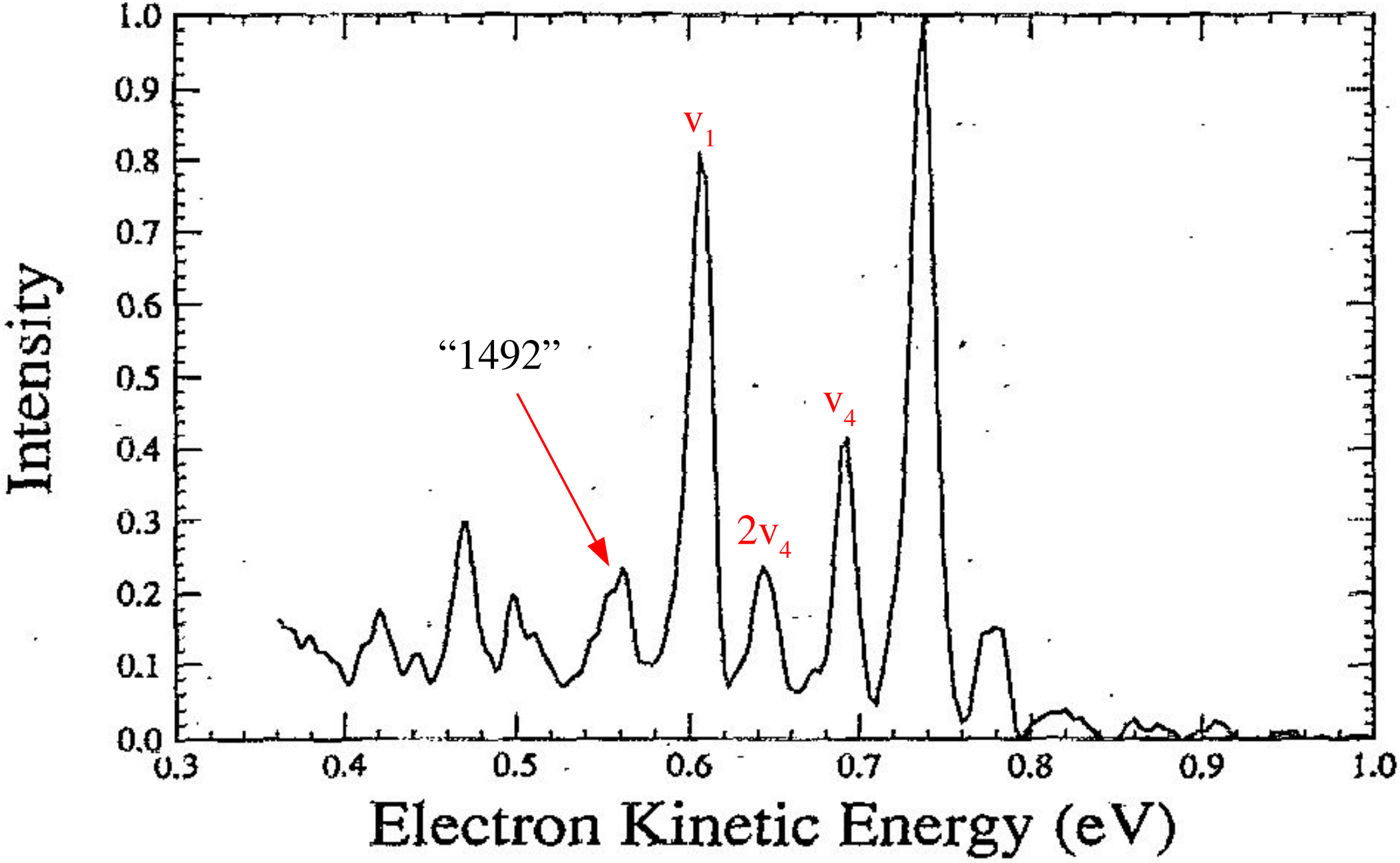


Simulation of Photodetachment at 450 K



Ground state dynamics of NO_3: Multimode vibronic borrowing including thermal effects

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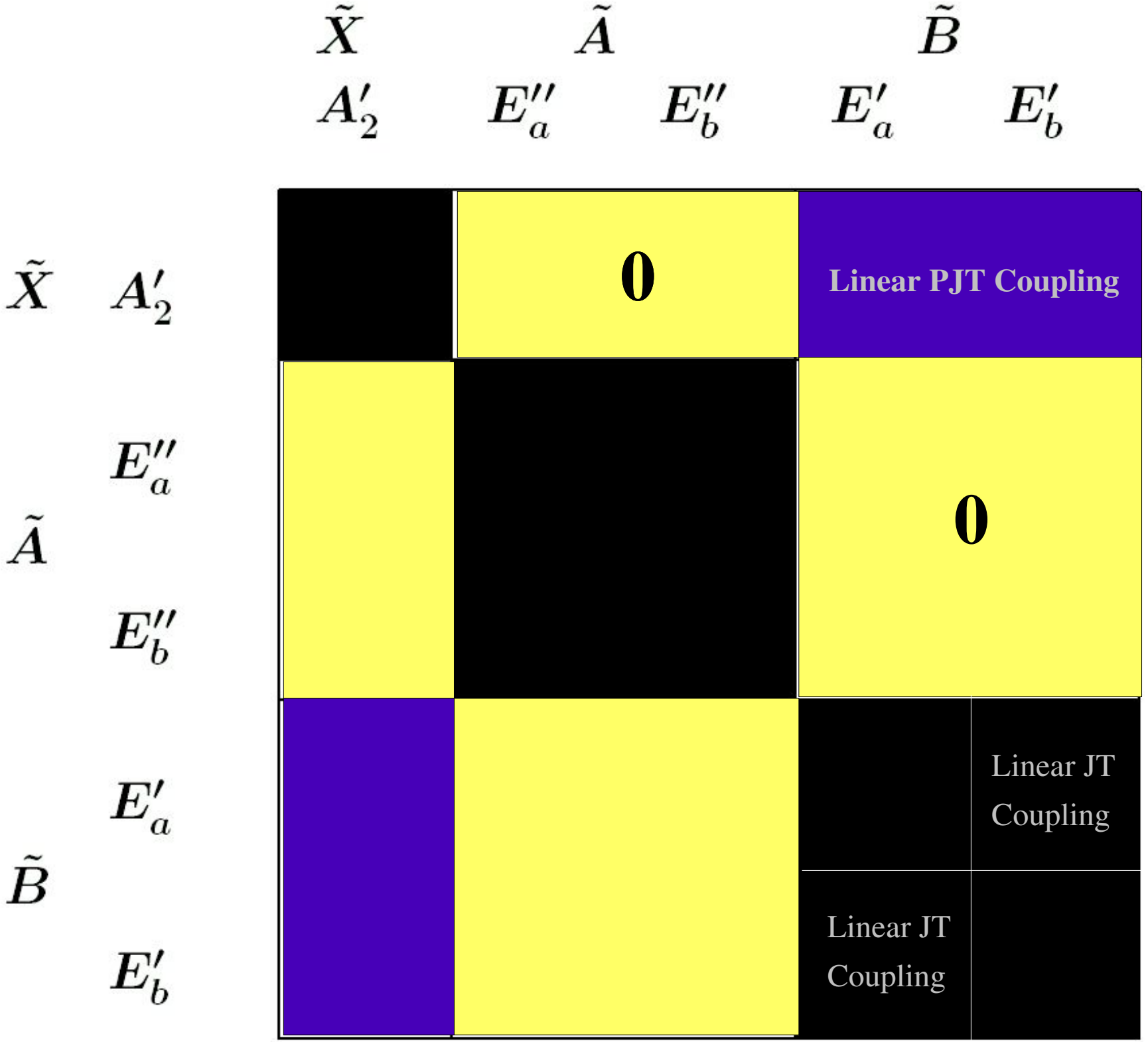
(Received 6 May 1993; accepted 27 August 1993)

TABLE II. The normal modes of NO_3^- and the corresponding experimentally measured frequencies (Ref. 47) as well as the values of the linear coupling constants we used in the dynamic calculation of the $X\,^2A_2'$ band.

	NO_3^- normal vibrations			Linear coupling constants (eV)		
Mode	Symm. type	Coordinate	Frequency (eV)	Diagonal	PJT	JT
Symm. stretch	A_1'	q_s	0.131	$\lambda_{sa}=0.154$ $\lambda'_{se}=-0.026$		
Out of plane	A_2''	q_a	0.104			
Asymm. stretch	E'	q_{x_1}, q_{y_1}	0.171		$\lambda_{p1}=-0.352$	$\lambda'_{j1}=-0.007$
Asymm. bend	E'	q_{x_2}, q_{y_2}	0.088		$\lambda_{p2}=0.164$	$\lambda'_{j2}=0.104$


$\tilde{X}$
$\tilde{A}$
$\tilde{B}$
A_2'
E_a''
E_b''
E_a'
E_b'
0
Linear PJT Coupling
0
Linear JT Coupling
Linear JT Coupling

Computational Details

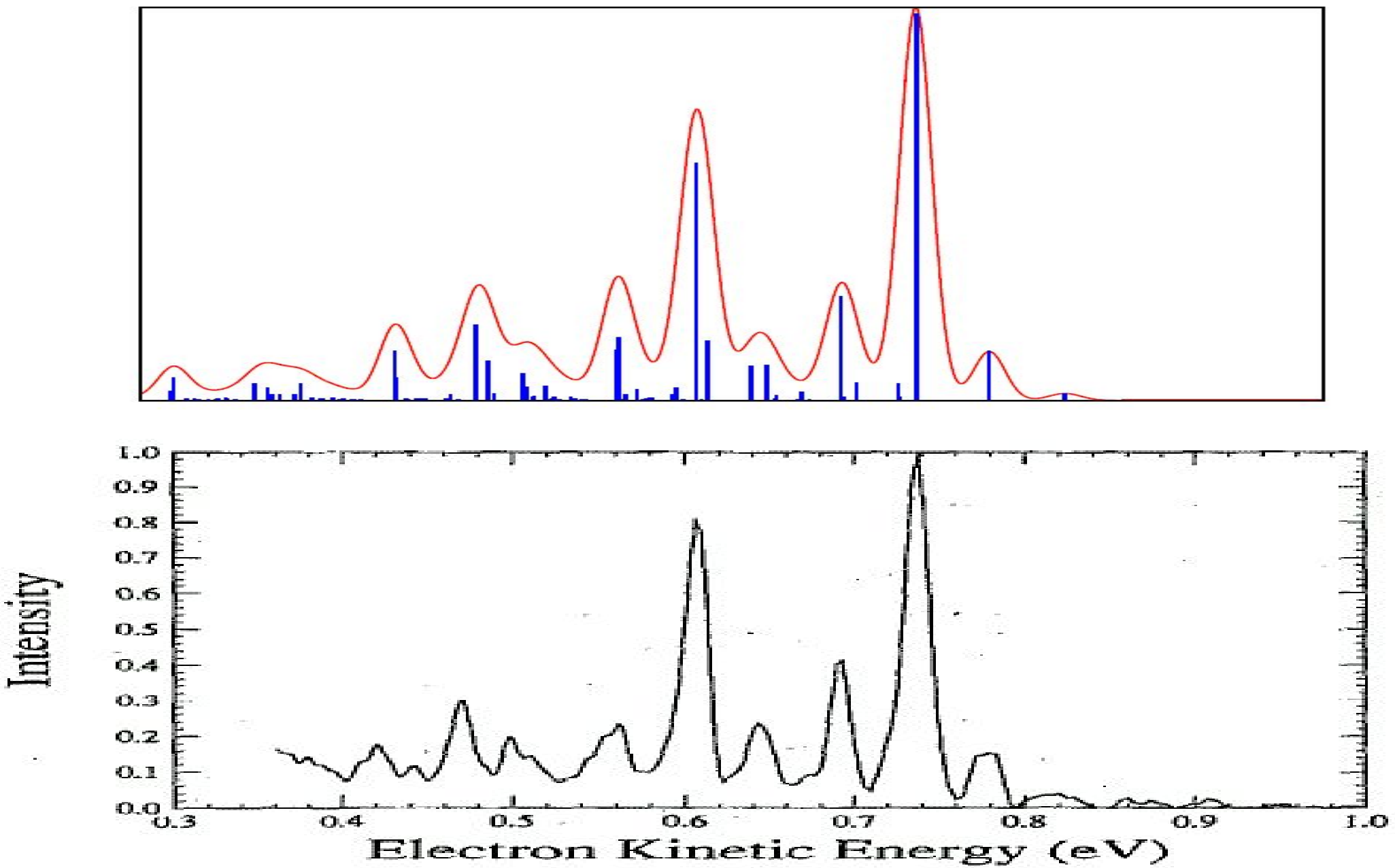
Direct product basis including three electronic states and five vibrational coordinates

9.6 million basis functions

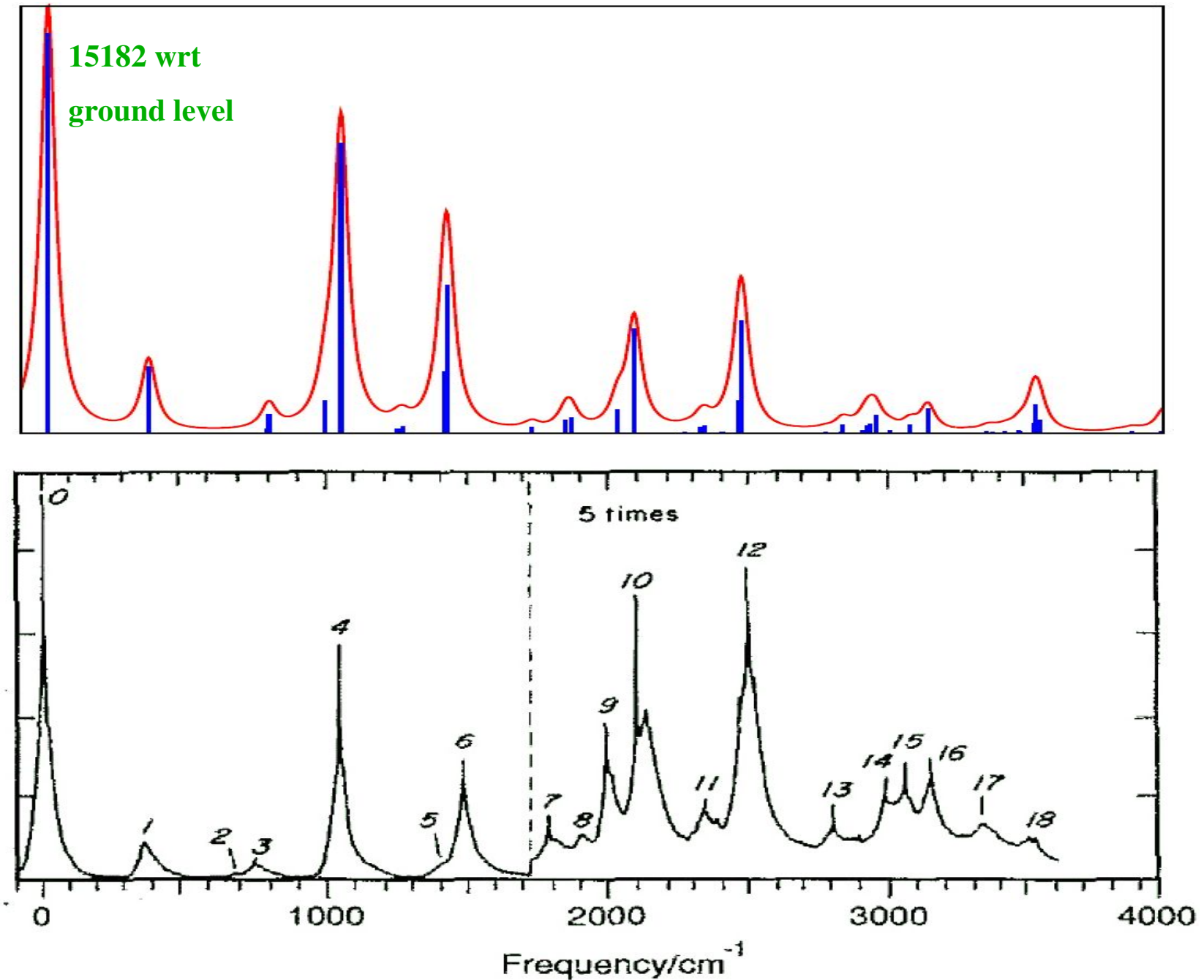
Haller *et al.* Hamiltonian used without any changes

Coordinates: Reduced normal coordinates of nitrate anion

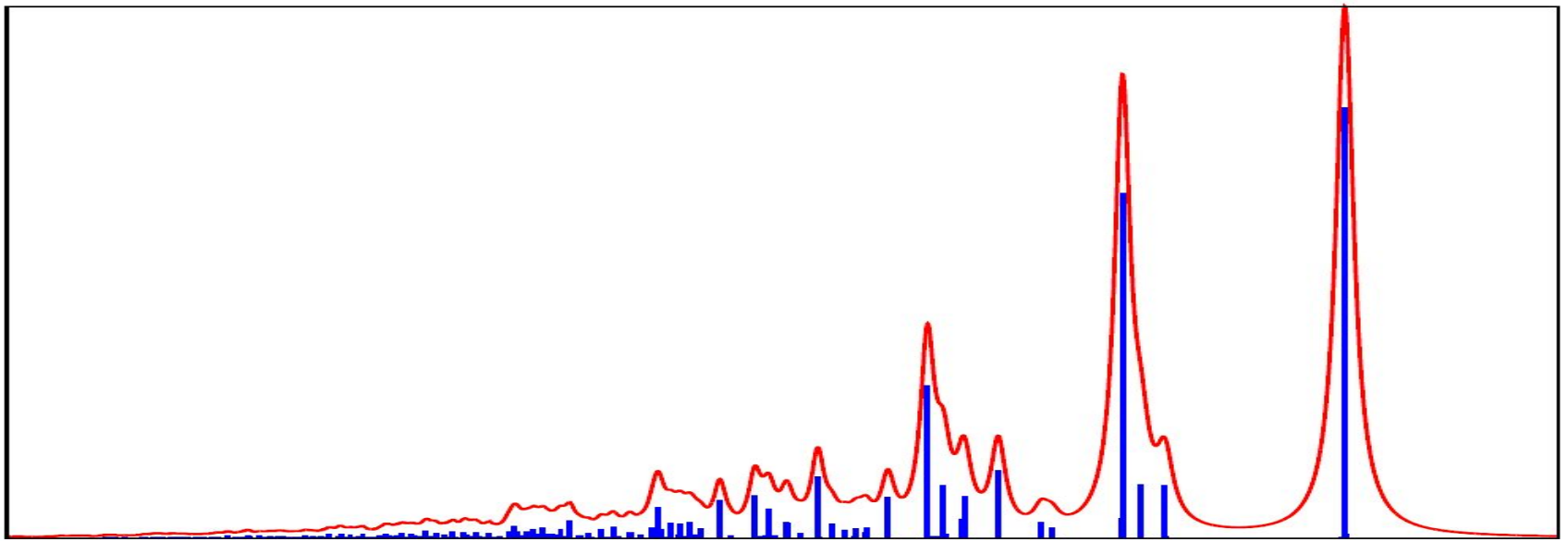
Simulation of NO_3^- Photodetachment Spectrum to $\tilde{X}$ State

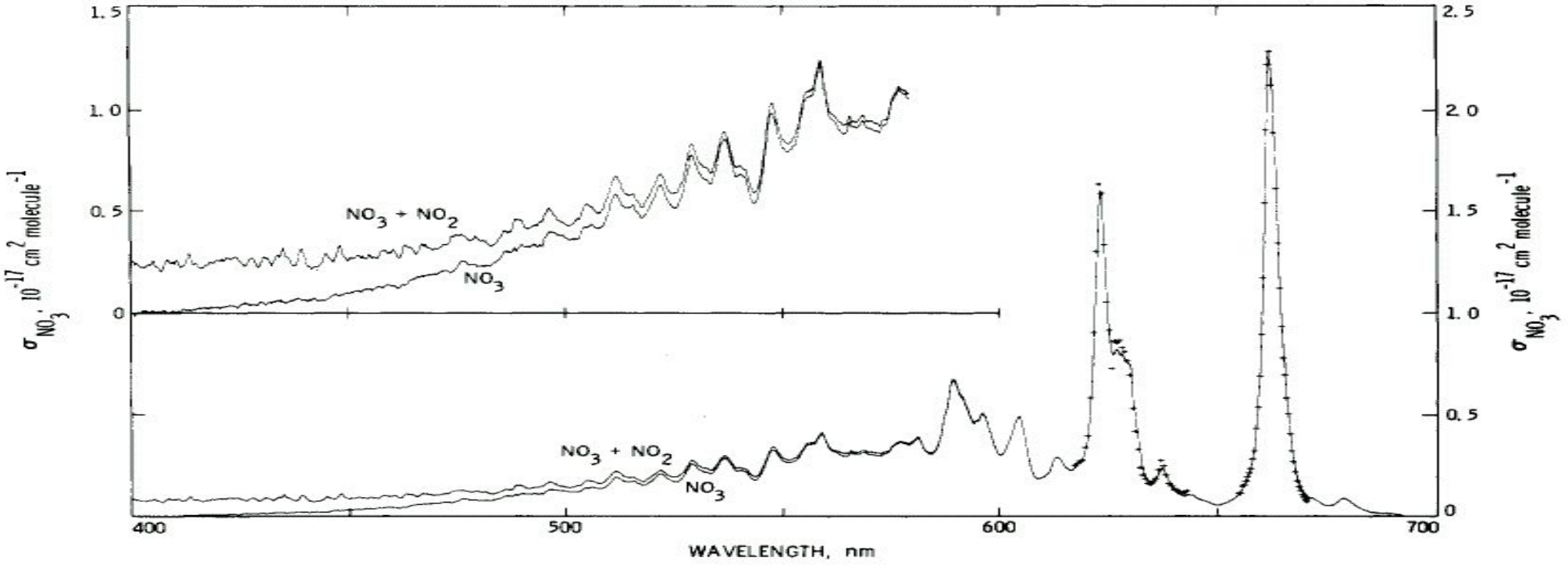


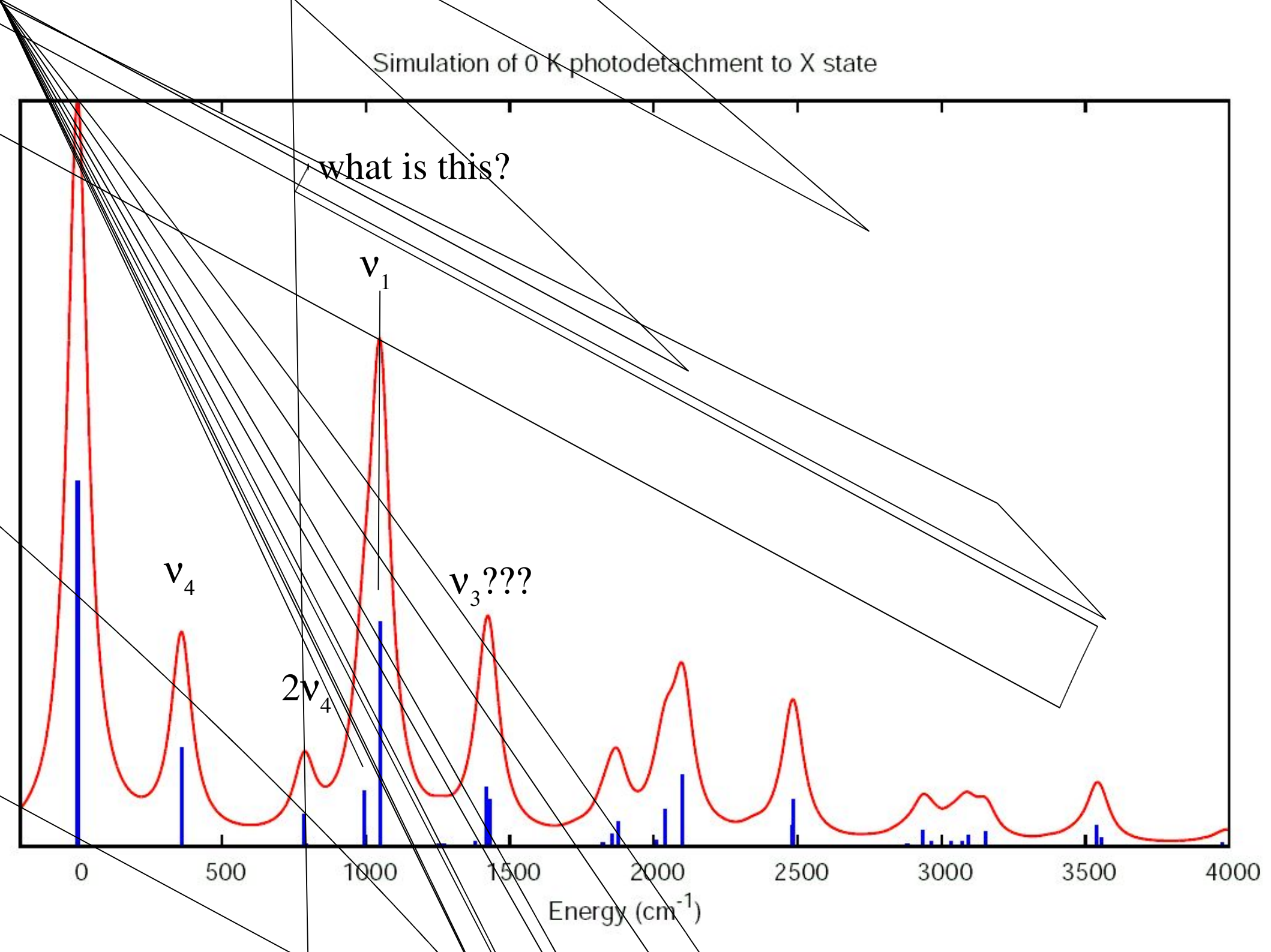
Simulation of 15109 cm^{-1} dispersed fluorescence of NO_3 ($\tilde{X} \leftarrow \tilde{B}$)



Simulation of $\tilde{X} \rightarrow \tilde{B}$ Absorption Spectrum of NO_3






Simulation of 0 K photodetachment to X state
what is this?
ν_1
ν_4
$2\nu_4$
ν_3???
0
500
1000
1500
2000
2500
3000
3500
4000
Energy (cm^{-1})

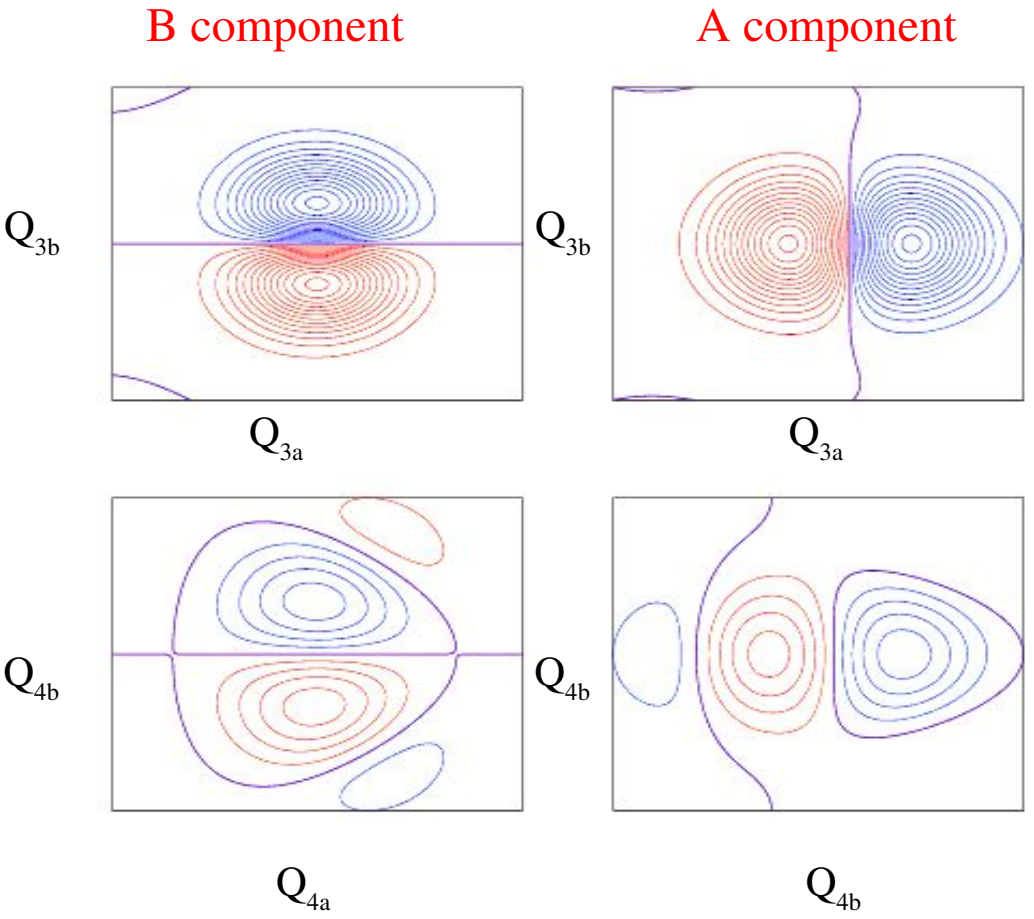
What is the nature of the 995 cm^{-1} feature?

Relatively weak in both DF and PES spectra

Overlaps with strong ν_1 feature

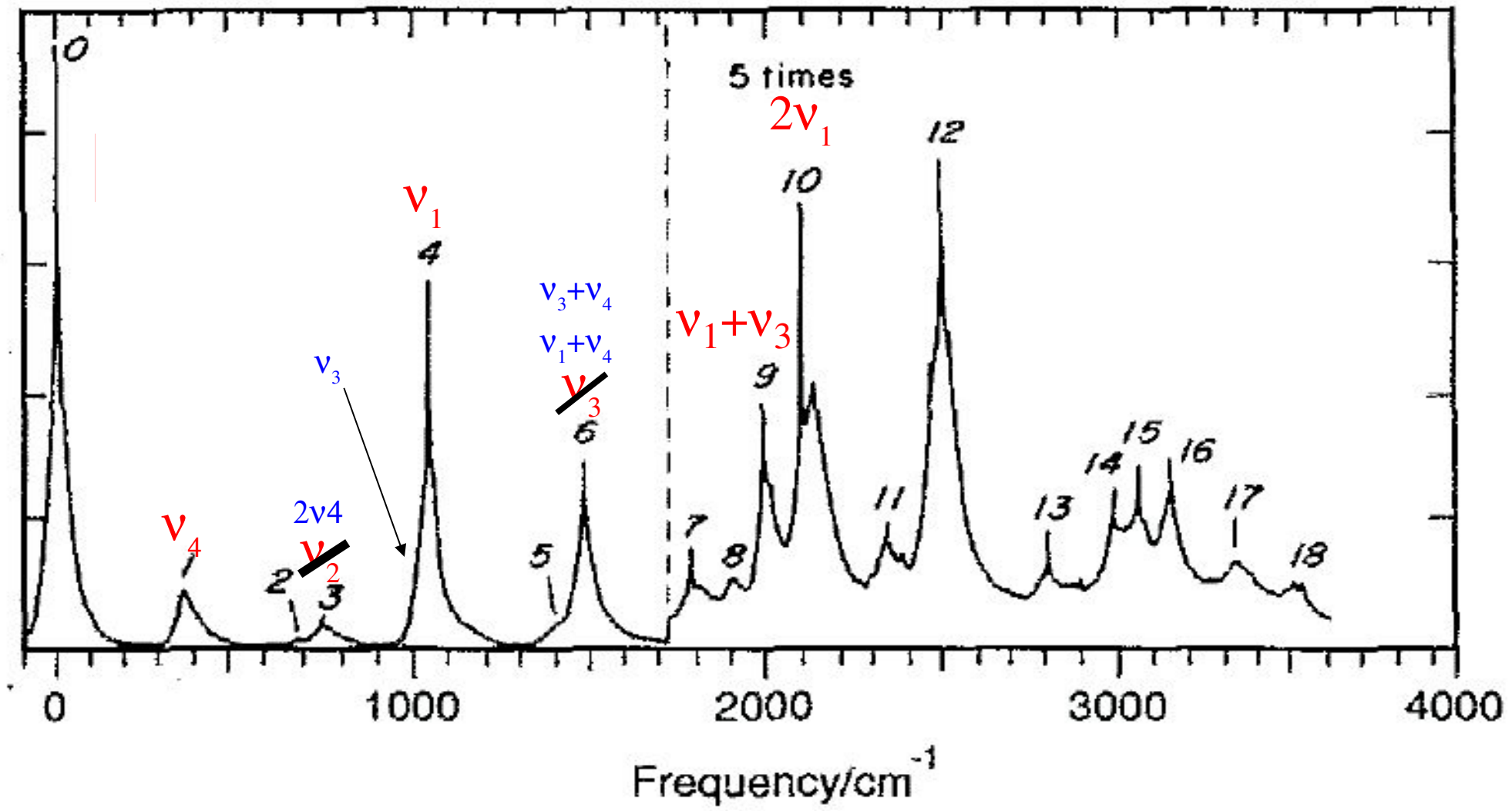
Degenerate level

Examine nodal structure of wavefunction



ν_3!!!!

Tentative Reassignment of DF Spectrum



Conclusions

LVC Hamiltonian reproduces electronic spectrA of NO_3 very well.

Common assignment of 1492 cm^{-1} feature to ν_3 needs to be reinvestigated.

Clumps of peaks at 2000, 3000 cm^{-1} might be due to polyads involving ν_1, ν_4.

Future Work

Attempt to assignment prominent features above 1500 cm^{-1} in terms of vibrational quantum numbers.

Work out vibrational assignments in the B state from simulation of absorption spectrum.

Extend model Hamiltonian approach to further analyze dark state spectrum obtained by Okumura and coworkers.

Acknowledgments

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Audrey and Juliet Stanton

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