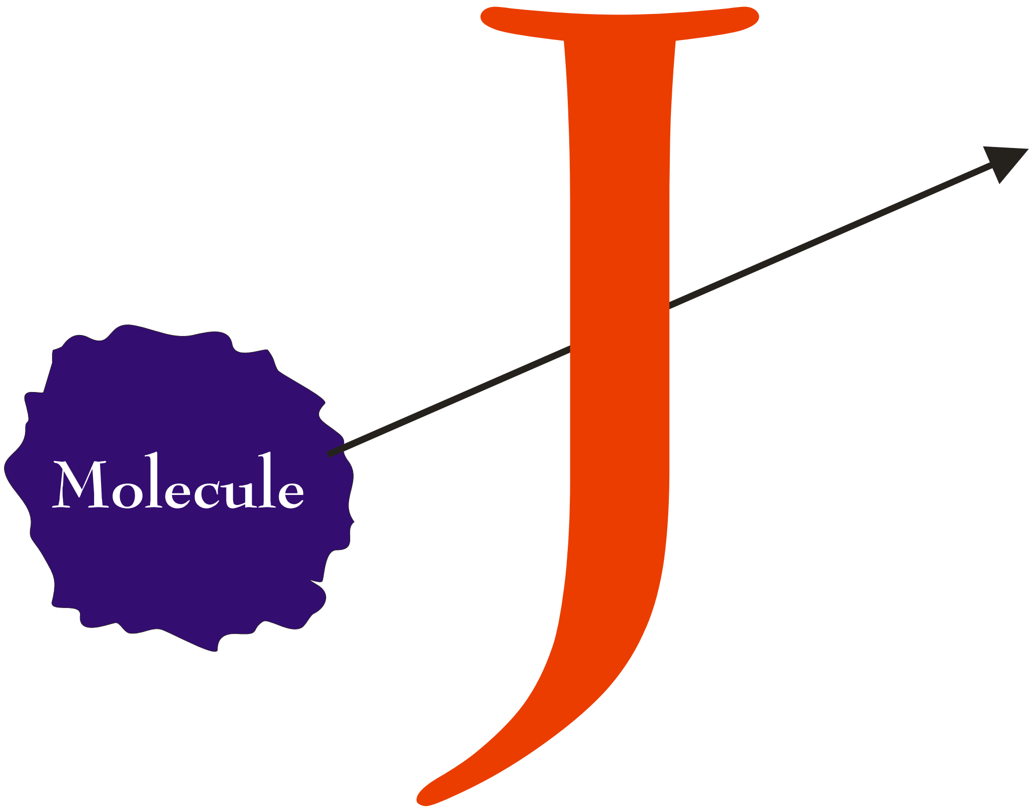
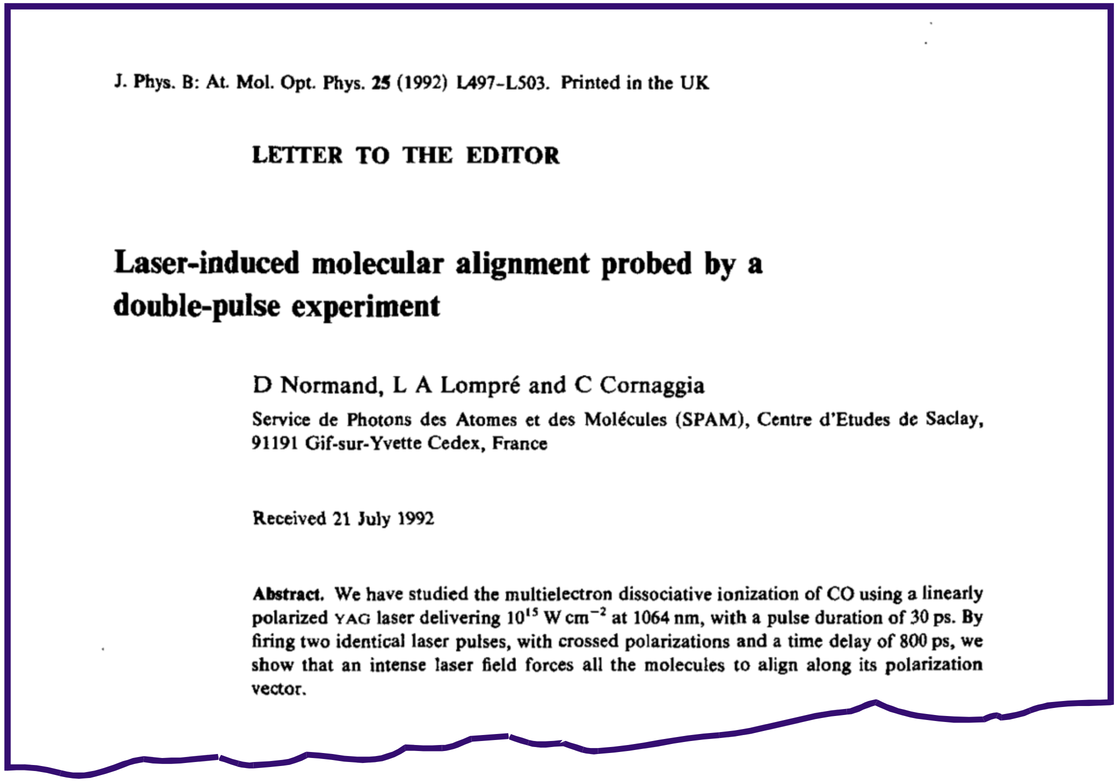
Molecules undergoing extreme rotation



$$\boxed{J \sim 10^2 \quad \text{or} \quad 10^3}$$



J. Phys. B: At. Mol. Opt. Phys. **25** (1992) L497–L503. Printed in the UK

LETTER TO THE EDITOR

Laser-induced molecular alignment probed by a double-pulse experiment

D Normand, L A Lompré and C Cornaggia

Service de Photons des Atomes et des Molécules (SPAM), Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France

Received 21 July 1992

Abstract. We have studied the multielectron dissociative ionization of CO using a linearly polarized YAG laser delivering 10^{15} W cm^{-2} at 1064 nm, with a pulse duration of 30 ps. By firing two identical laser pulses, with crossed polarizations and a time delay of 800 ps, we show that an intense laser field forces all the molecules to align along its polarization vector.

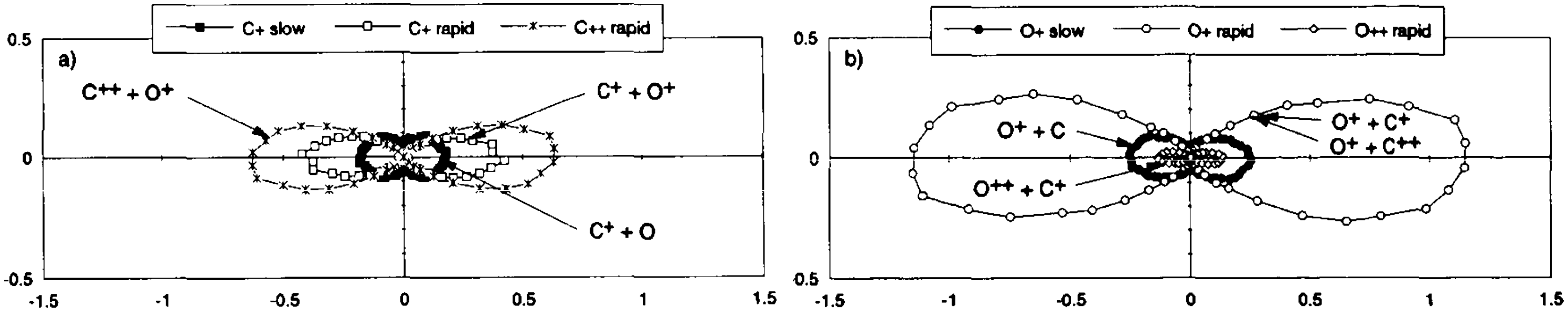
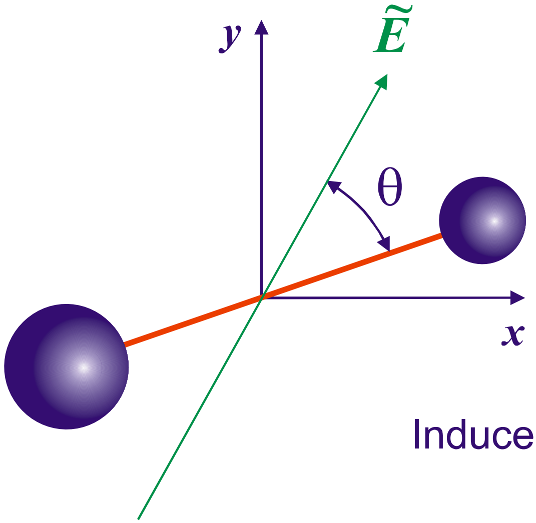
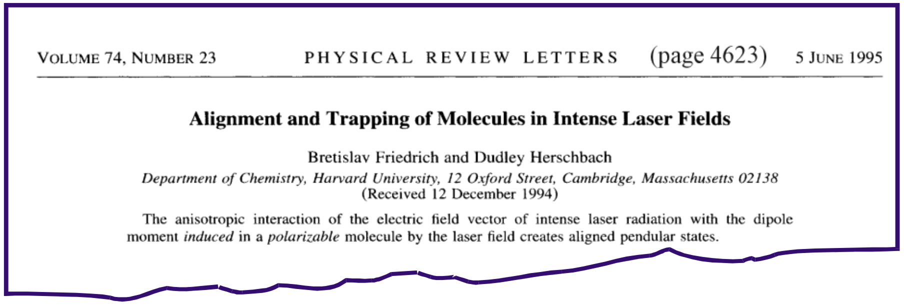


Figure 2. Angular distribution of the main fragments observed in the Multi Electron Dissociative Ionization (MEDI) of CO




Volume 74, Number 23 PHYSICAL REVIEW LETTERS (page 4623) 5 June 1995

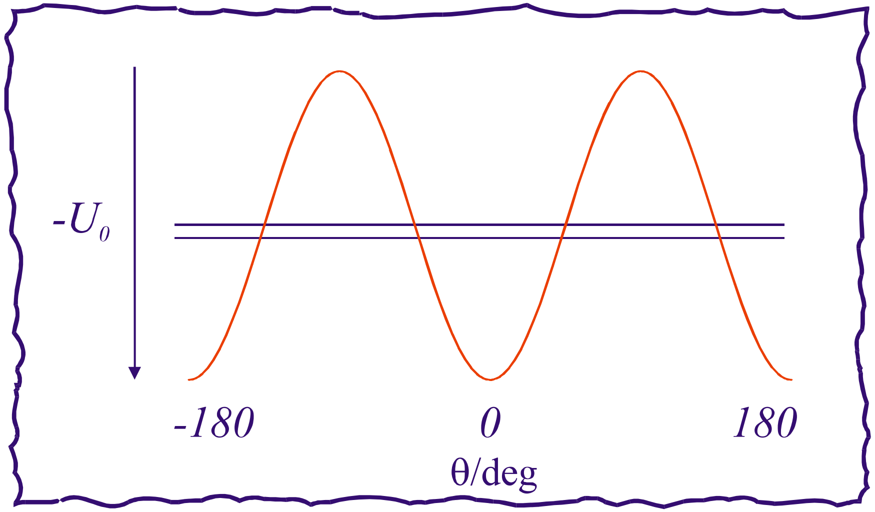
Alignment and Trapping of Molecules in Intense Laser Fields

Bretislav Friedrich and Dudley Herschbach
Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138
(Received 12 December 1994)

The anisotropic interaction of the electric field vector of intense laser radiation with the dipole moment *induced* in a *polarizable* molecule by the laser field creates aligned pendular states.

Induced dipole moment (over laser cycle) interacts with $\tilde{E}$

$$\boxed{V(\theta) = -\underbrace{\left[\frac{1}{4}(\alpha_\parallel - \alpha_\perp)E^2\right]}_{U_0\approx 50\mathrm{meV}}\cos^2\theta}$$



Pendular states

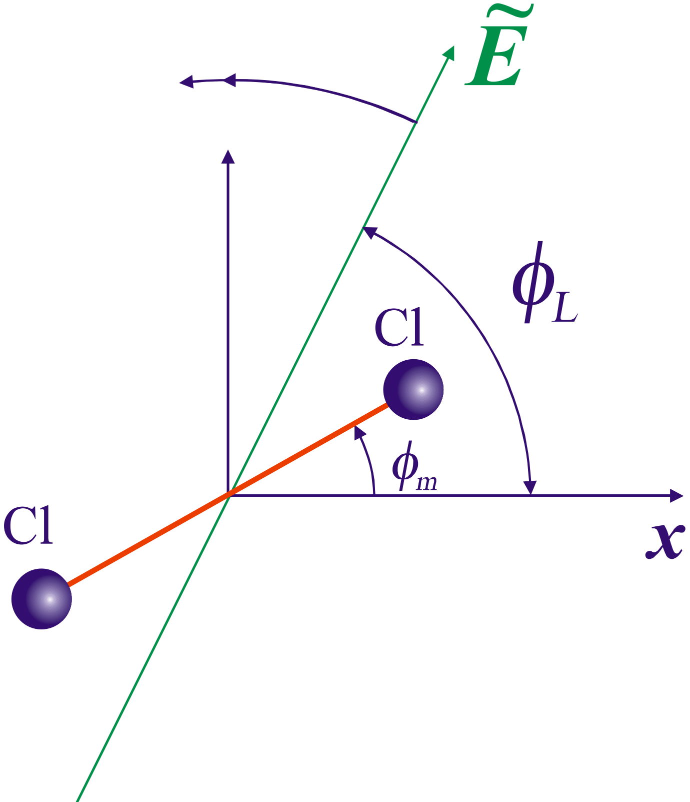
$\xcancel{J}$

Angular trap

Rotate the angular trap ⟶ GIVES BIG J

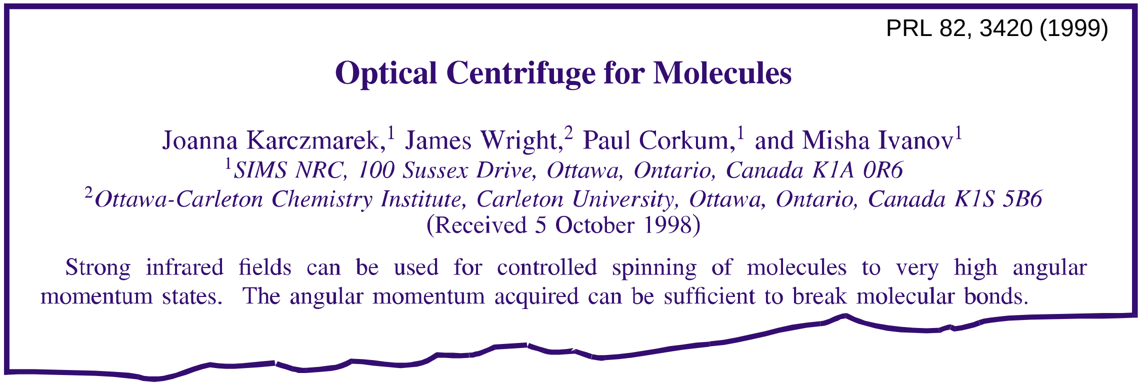
$$\boxed{\phi_L(t) = \beta t^2/2}$$

Constant acceleration



Rotation frequency

$$\Omega = \dot{\phi}_L = \beta t$$

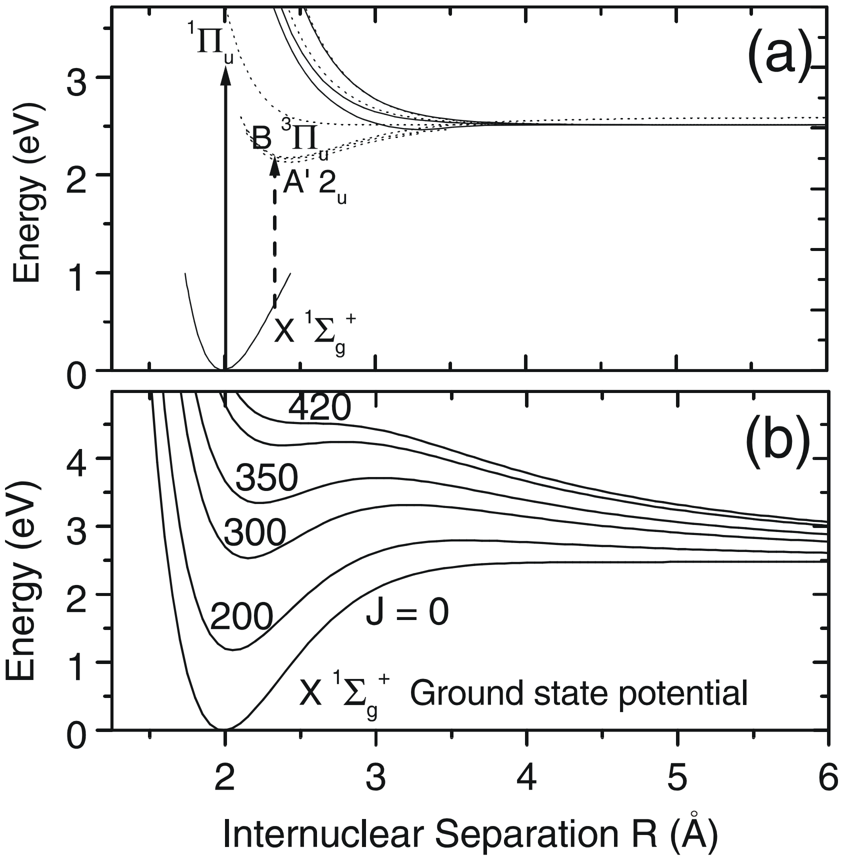

PRL 82, 3420 (1999)

Optical Centrifuge for Molecules

Joanna Karczmarek,[1] James Wright,[2] Paul Corkum,[1] and Misha Ivanov[1]
[1]*SIMS NRC, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6*
[2]*Ottawa-Carleton Chemistry Institute, Carleton University, Ottawa, Ontario, Canada K1S 5B6*
(Received 5 October 1998)

Strong infrared fields can be used for controlled spinning of molecules to very high angular momentum states. The angular momentum acquired can be sufficient to break molecular bonds.

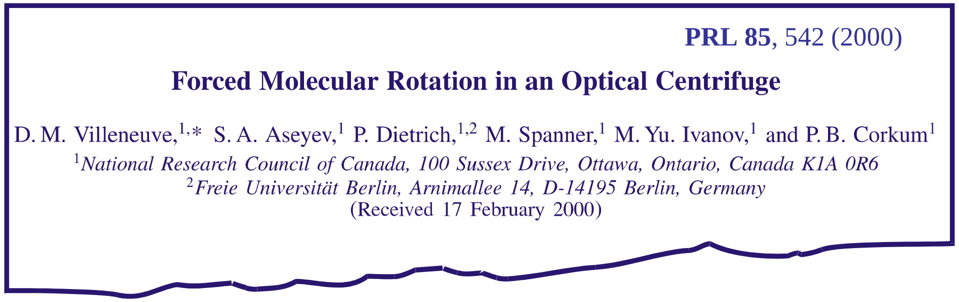
Forced rotation of Cl_2 in an Optical Centrifuge



Cl_2
$J=0$

Cl_2
Big J

$$V^J(R) = V^0(R) + B(R)J(J+1)$$

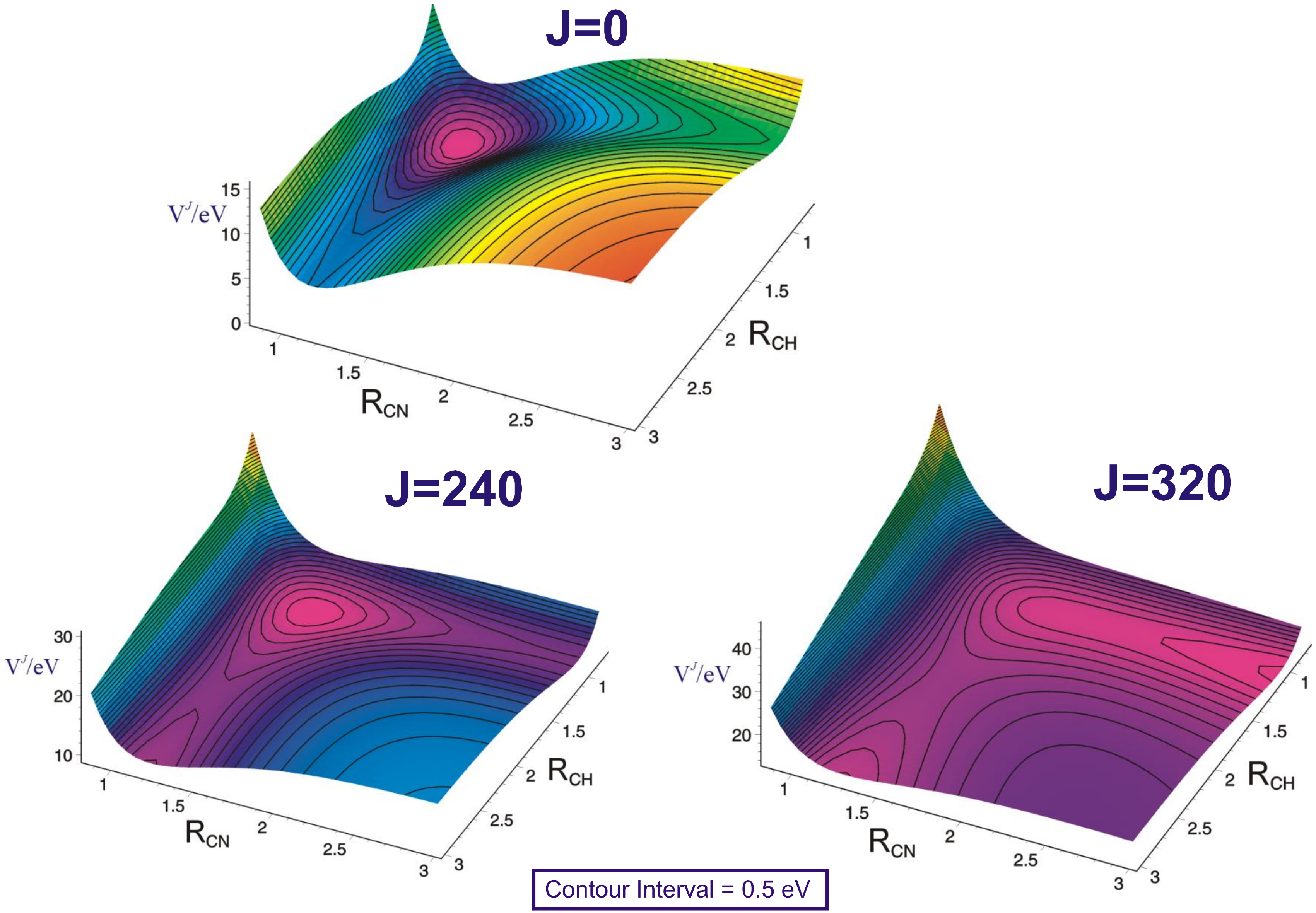


PRL 85, 542 (2000)

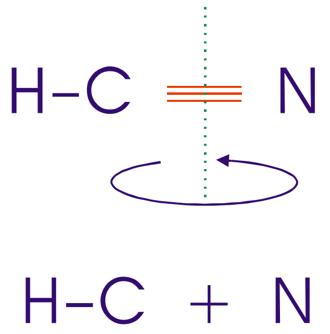
Forced Molecular Rotation in an Optical Centrifuge

D. M. Villeneuve,[1,*] S. A. Aseyev,[1] P. Dietrich,[1,2] M. Spanner,[1] M. Yu. Ivanov,[1] and P. B. Corkum[1]
[1]*National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6*
[2]*Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*
(Received 17 February 2000)

FOR LINEAR HCN: $V^J(R_{CH}, R_{CN}) = V^0(R_{CH}, R_{CN}) + B(R_{CH}, R_{CN})J(J+1)$



In Theory ....



At $J=0$

D_{CN} = 10.6 eV

D_{CH} = 5.7 eV

Using λ = 800nm. Pulse = 6 fs – coherent band with $\Delta\omega$ = 72 THz.

This gives $\Omega_{max}=\Delta\omega/2 > 20$ THz.

Need this for E_{rot} (classical) = $I\,\Omega^2/2 > D_{CN}$

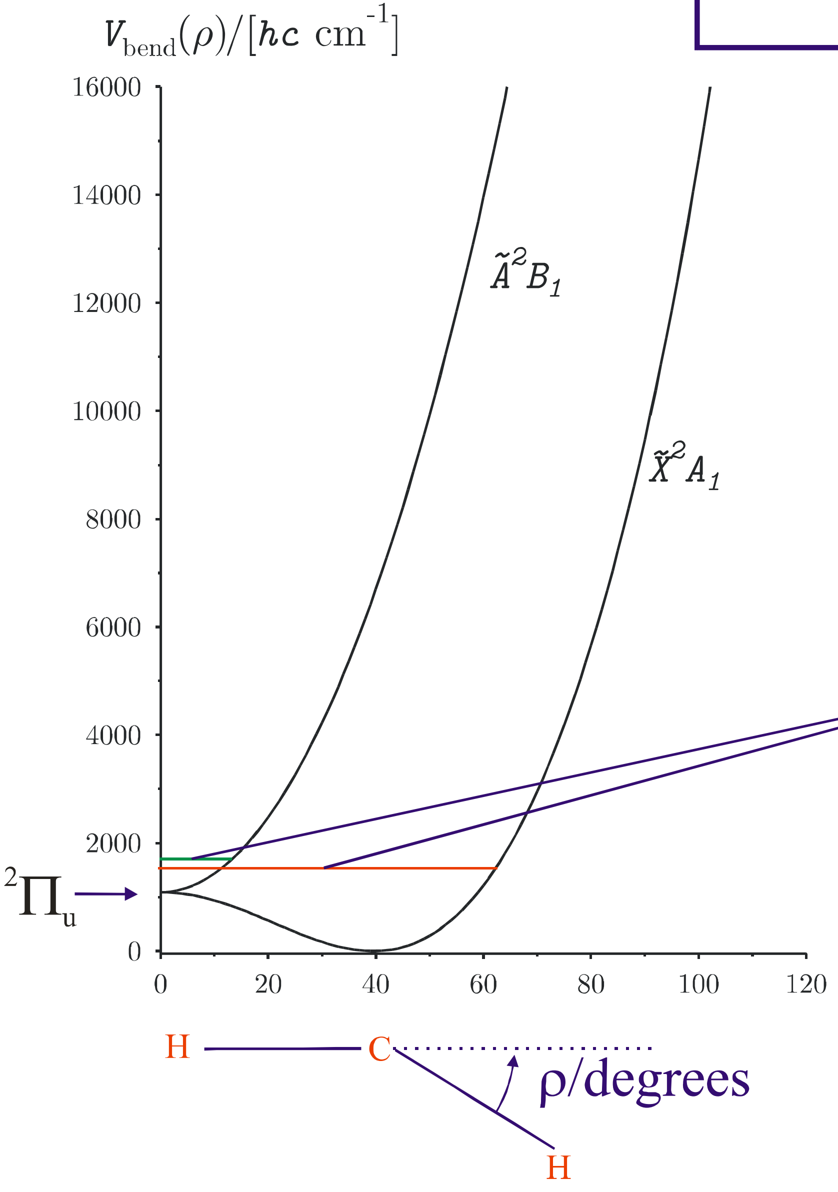
JCP 116, 10636 (2002)

Selective dissociation of the stronger bond in HCN using an optical centrifuge

R. Hasbani, B. Ostojić, P. R. Bunker, and M. Yu. Ivanov

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

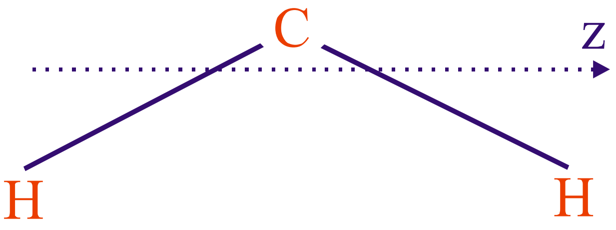
CH_2^+



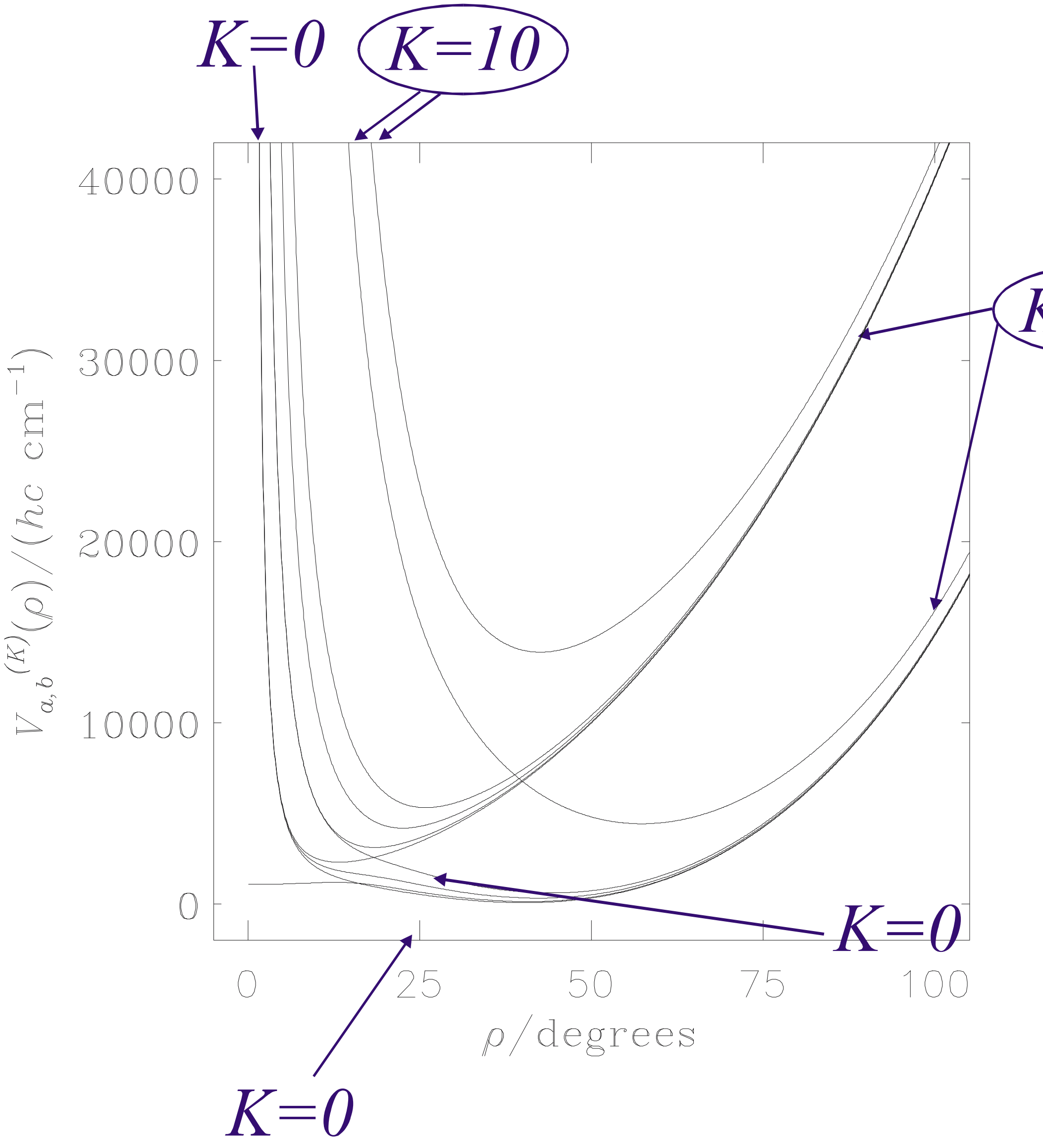
$T_e(\tilde{B}\ ^2A_2) \sim 7\text{eV}$

$T_e(\tilde{a}\ ^4A_2) \sim 4\text{eV}(\alpha_e = 77\,^\circ)$

$\hat{H}^{(z)}_{\text{rot}}$

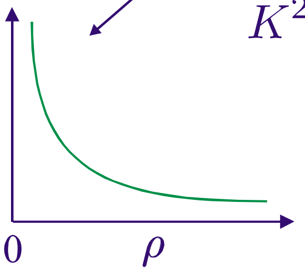


CH$_2^+$



$$\hat{H}^{(z)}_{\text{rot}} = A(\rho)\left[\hat{N}_z - \hat{L}_z\right]^2$$

$$= A(\rho)\left[\hat{N}_z^2 + 2\hat{N}_z\hat{L}_z + \hat{L}_z^2\right]$$



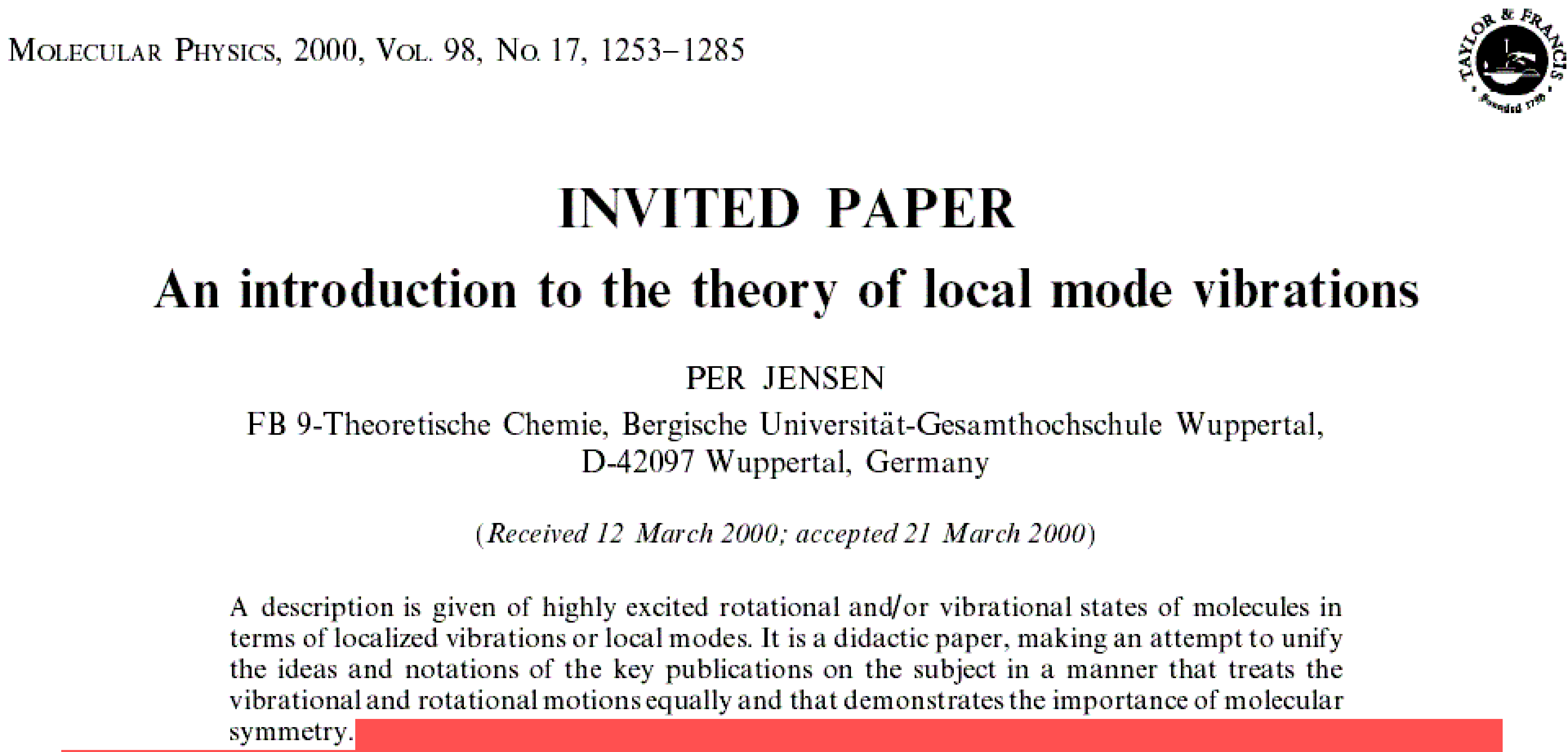
K^2

$$\underbrace{-2K\langle\tilde{X}|\hat{L}_z|\tilde{A}\rangle}_{i\Lambda}$$

$\langle\hat{L}_z^2\rangle \sim \Lambda^2$

Rotational Energy Level Clusters

1972	Dorney and Watson	CH_4 8-fold and 6-fold clusters
1978	Zhilinskii and Pavlichenkov	H_2O 4-fold clusters (E_{rb})
1978	Harter and Patterson	Rotational energy surfaces and clusters
1991	Lehmann	Local mode theory and clusters
1992	Kozin et al	H_2Se 4-fold clusters observed
1993	Kozin and Jensen	H_2Se 4-fold cluster theory (E_{rbs})
1994	Jensen and Bunker	H_2X 4-fold cluster symmetry
1996	Kozin et al	H_2Te 4-fold clusters (exp and theory)
1997	Jensen et al	Review paper on 4-fold clusters
2000	Jensen	Review paper on LMT and clusters



MOLECULAR PHYSICS, 2000, VOL. 98, NO. 17, 1253–1285

INVITED PAPER

An introduction to the theory of local mode vibrations

PER JENSEN

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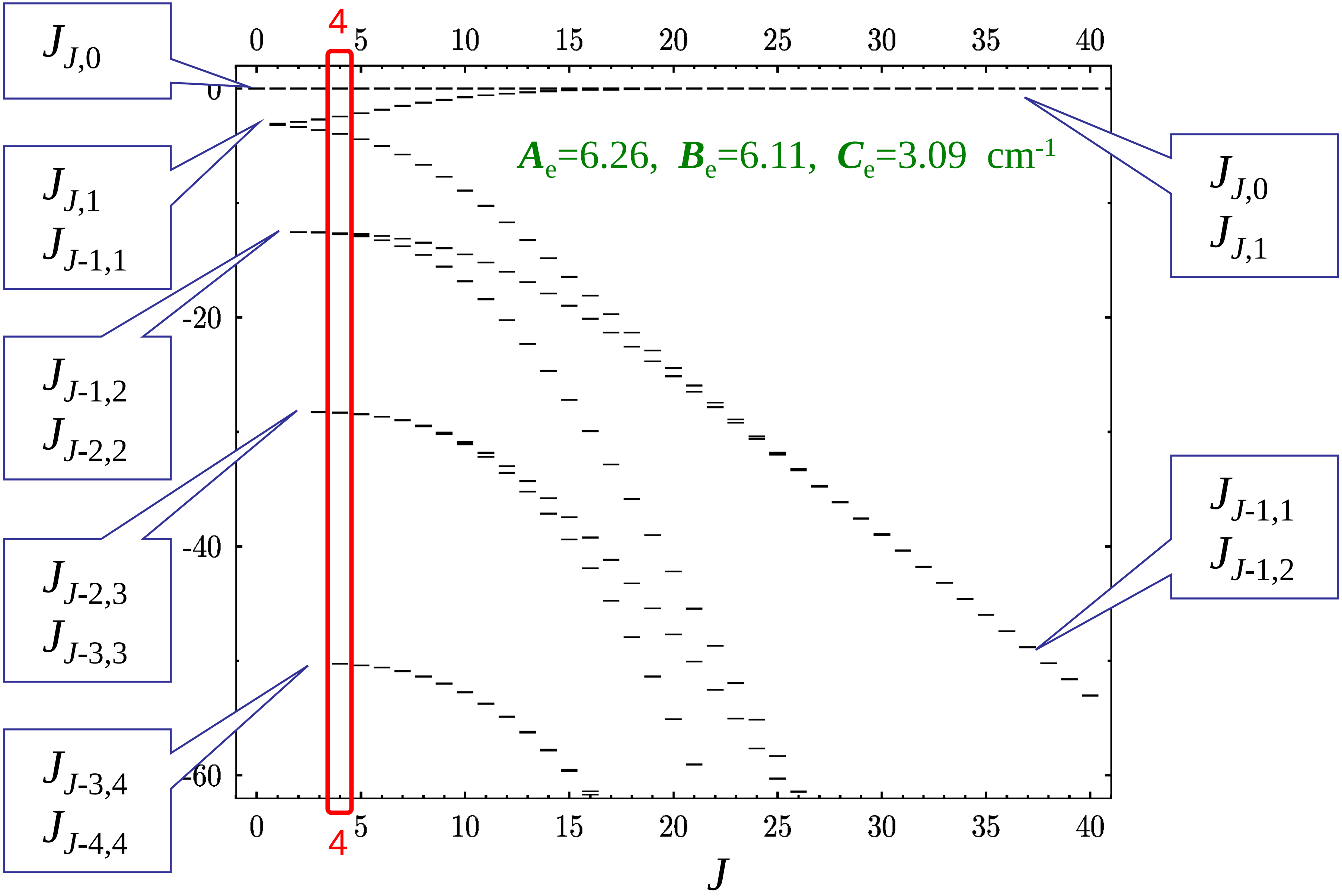
(*Received 12 March 2000; accepted 21 March 2000*)

A description is given of highly excited rotational and/or vibrational states of molecules in terms of localized vibrations or local modes. It is a didactic paper, making an attempt to unify the ideas and notations of the key publications on the subject in a manner that treats the vibrational and rotational motions equally and that demonstrates the importance of molecular symmetry.

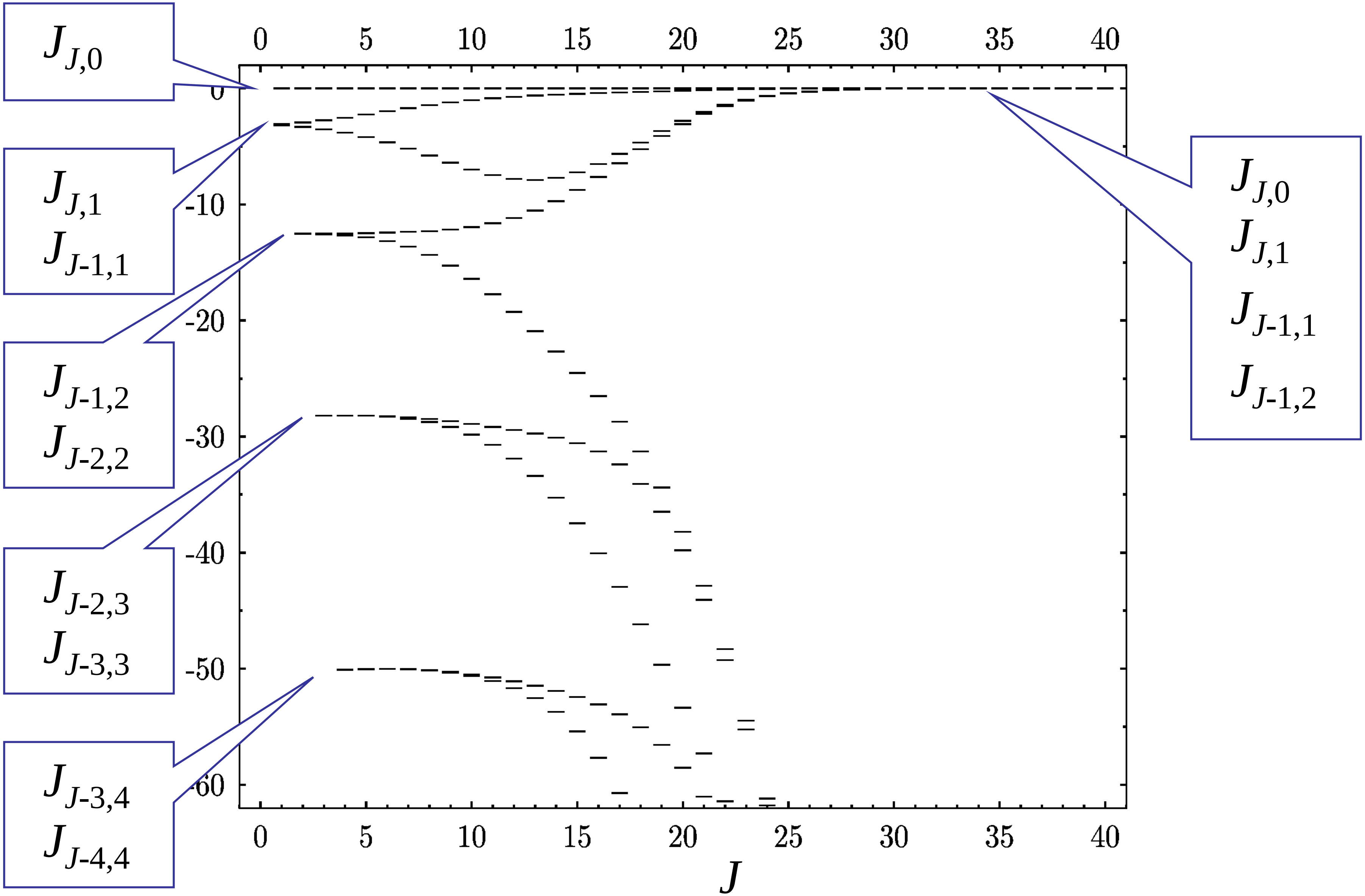
Emphasis is put on explaining the intimate relationship between local mode vibrations and the formation of both vibrational and rovibrational energy level clusters.

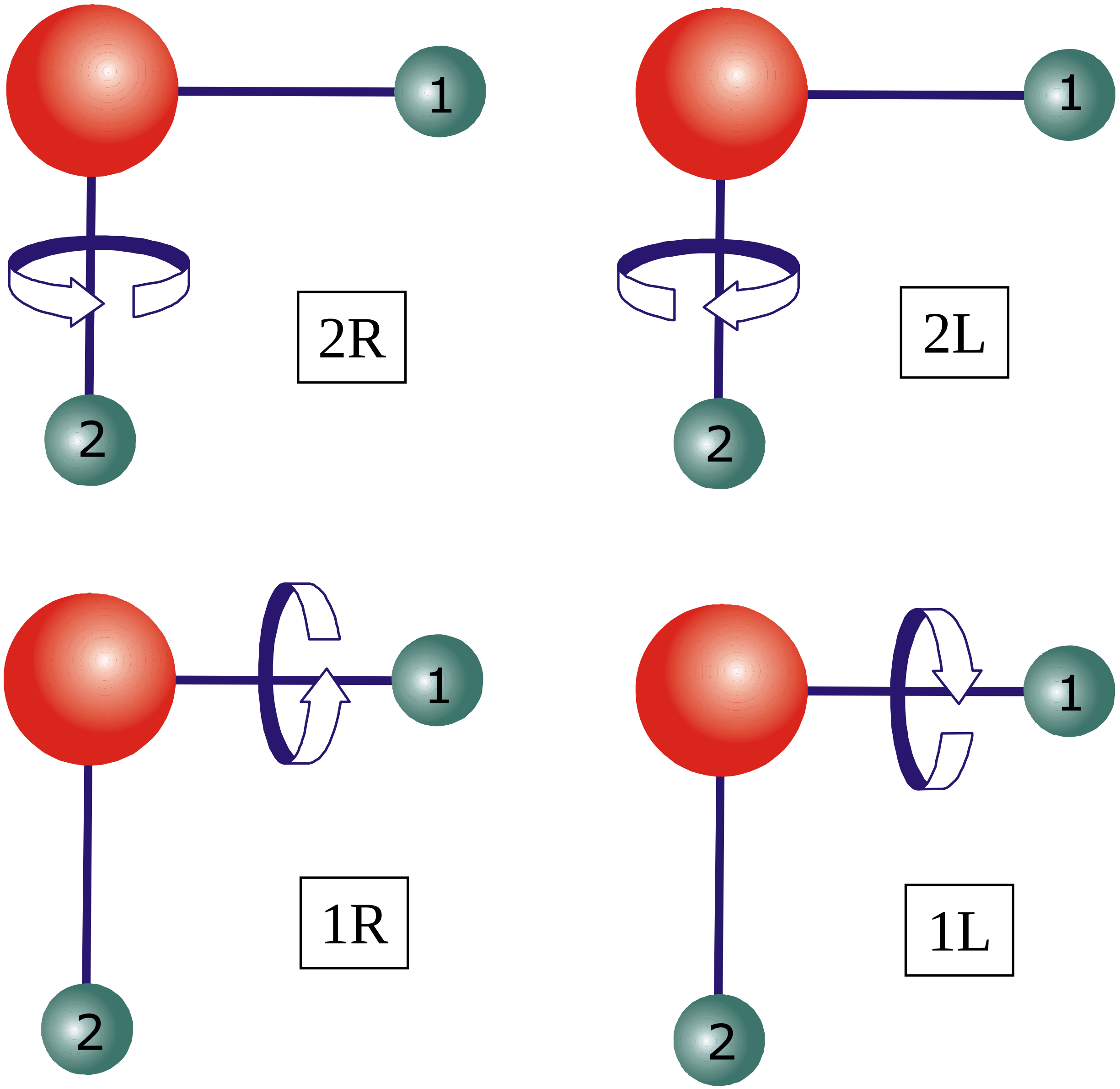
H_2Te Rigid Rotor Energy Levels [$E(J_{KaKc})$-$E(J_{J0})$]



A_e=6.26, B_e=6.11, C_e=3.09 cm^{-1}

Actual H_2Te Energy Levels $[E(J_{KaKc})-E(J_{J0})]$

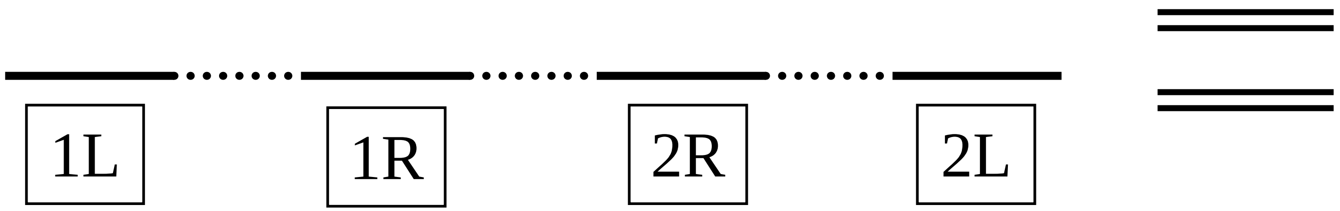




$$\left.\begin{array}{l} J_{J,0} \\ J_{J,1} \\ J_{J-1,1} \\ J_{J-1,2} \end{array}\right\} \equiv$$

$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in} \quad \boldsymbol{C}_{2\text{v}}(\text{M})$$

Kinetic Tunneling



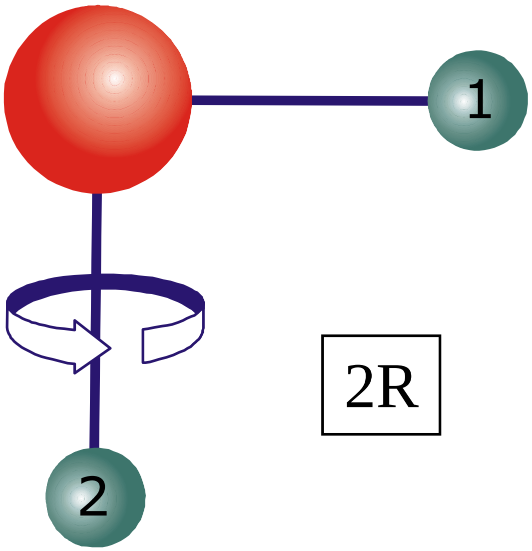
J even	*J* odd
A_1	B_2
B_1	A_2
A_2	B_1
B_2	A_1

We can write

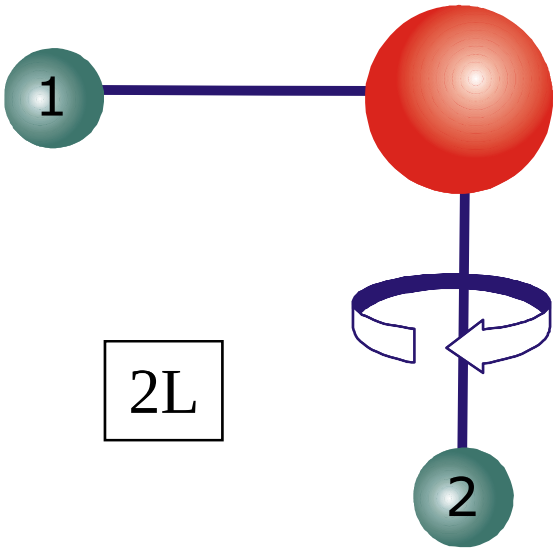
$$|1R\rangle = \frac{1}{2}(|A_1\rangle + |A_2\rangle + |B_1\rangle + |B_2\rangle)$$

For one form (12), *E**, and (12)* are not feasible. “A dynamical barrier”.

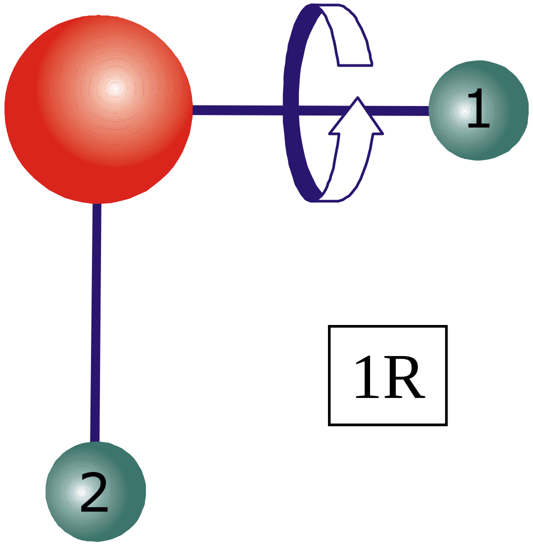
Thus the MS group is just {*E*} for each form and it must be chiral.



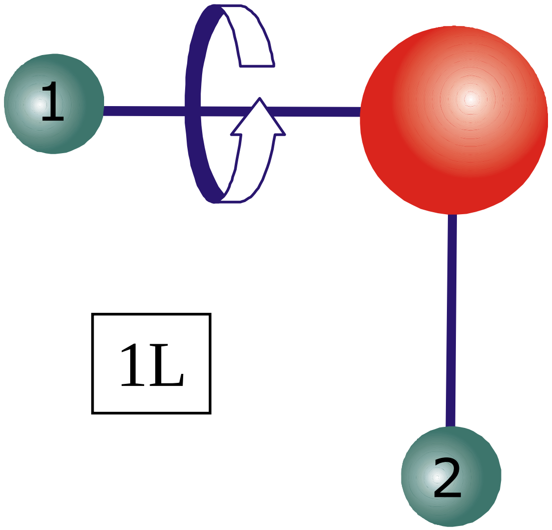
2R



2L



1R



1L

WHAT ARE THE LIFETIMES OF SUCH “DYNAMICALLY” CHIRAL STATES at *t*=0

$$|\mathbf{1}\boldsymbol{R}\rangle = \frac{\mathbf{1}}{\mathbf{2}}(|\boldsymbol{A}_{\mathbf{1}}\rangle + |\boldsymbol{A}_{\mathbf{2}}\rangle + |\boldsymbol{B}_{\mathbf{1}}\rangle + |\boldsymbol{B}_{\mathbf{2}}\rangle)$$

Using

$$i\,\hbar\frac{\partial|t\rangle}{\partial t} = \widehat{H}_{\mathrm{rv}}\,|t\rangle$$

at time *t*

$$|1\mathrm{R};t\rangle = \frac{1}{2}\left(\sum_{\Gamma} e^{-i\frac{E_{\Gamma}\,t}{\hbar}}\,|\Gamma\rangle\right)$$

Probability of being in |1R> at time *t* is:

$$|\langle 1\mathrm{R}|1\mathrm{R};t\rangle|^2 = \frac{1}{16}\left|\sum_{\Gamma=A_1,A_2,B_1,B_2} e^{-i\frac{(E_\Gamma-\bar{E})\,t}{\hbar}}\right|^2$$

For high *J*:

i.e. $(E_\Gamma - \bar{E}) = \pm\frac{\Delta_J}{2}$

$$|\langle 1\mathrm{R}|1\mathrm{R};t\rangle|^2 = \cos^2\left(\frac{\Delta_J\,t}{2\,\hbar}\right)$$

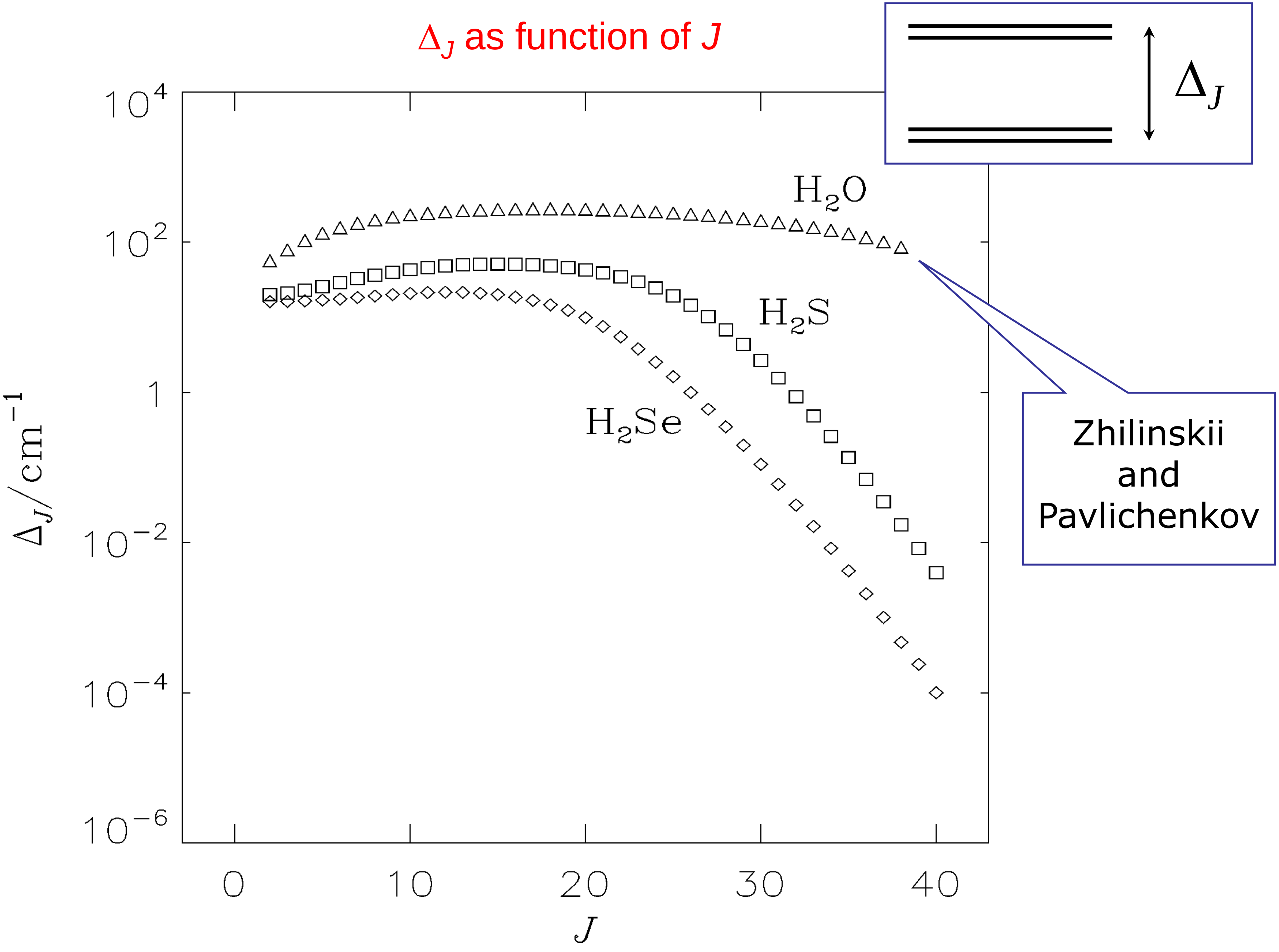
$$|\langle 1\mathrm{R}|1\mathrm{R};t\rangle|^2 = \cos^2\left(\frac{\Delta_J\, t}{2\,\hbar}\right)$$

Time for probability to have decreased to 1/2

(Half-life)

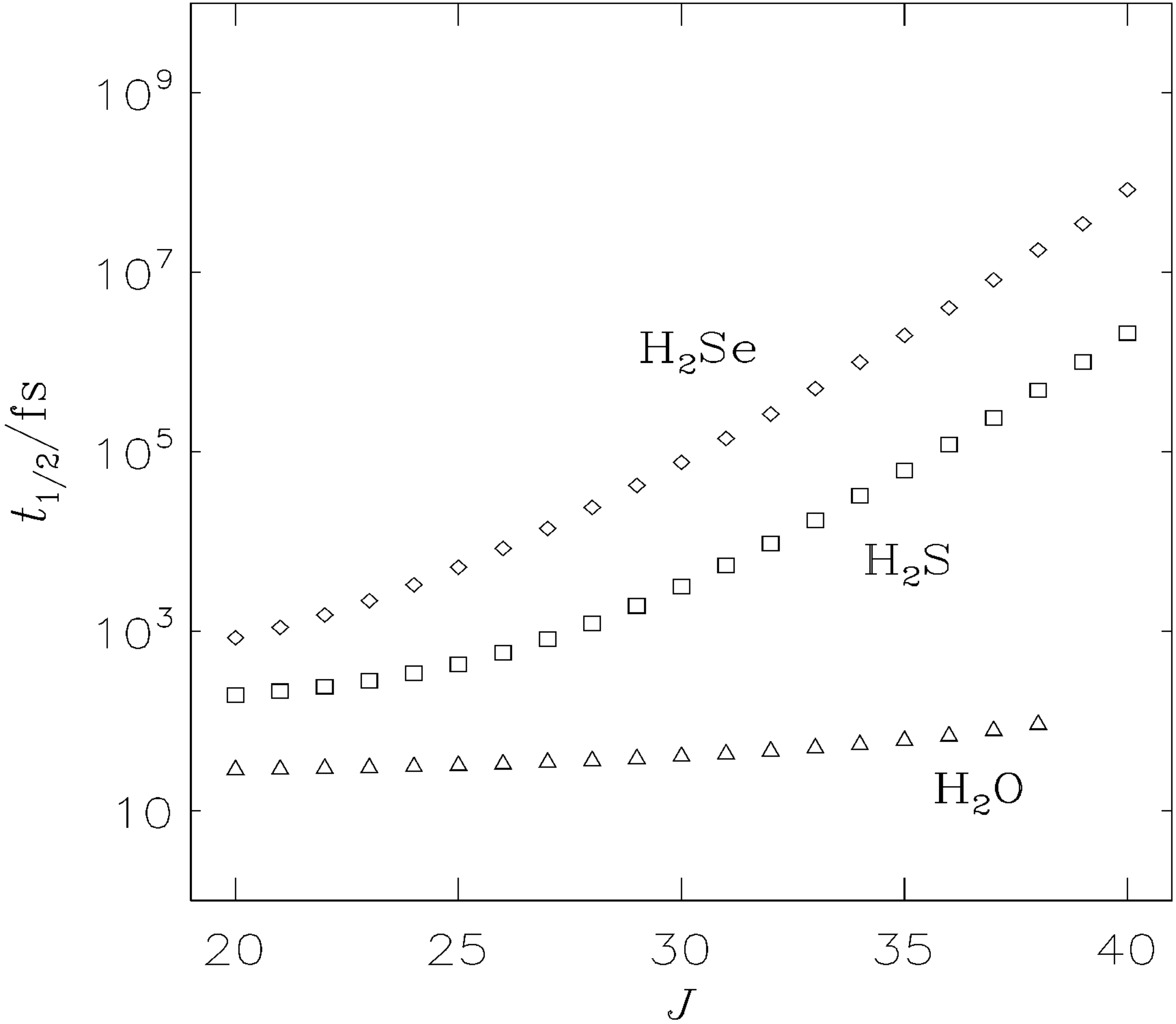
$$t_{1/2} = \frac{2\,\hbar}{\Delta_J}\arccos\left(\frac{1}{\sqrt{2}}\right) = \frac{h}{4\,\Delta_J}.$$

Δ_J as function of J

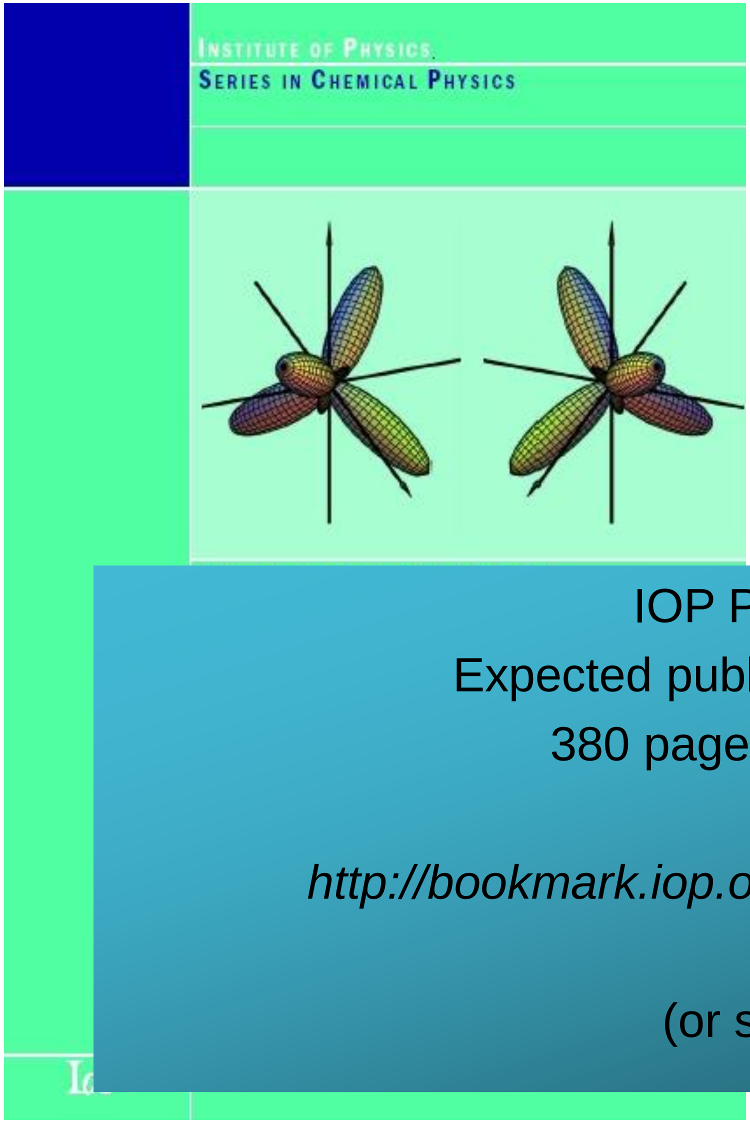


Zhilinskii and Pavlichenkov

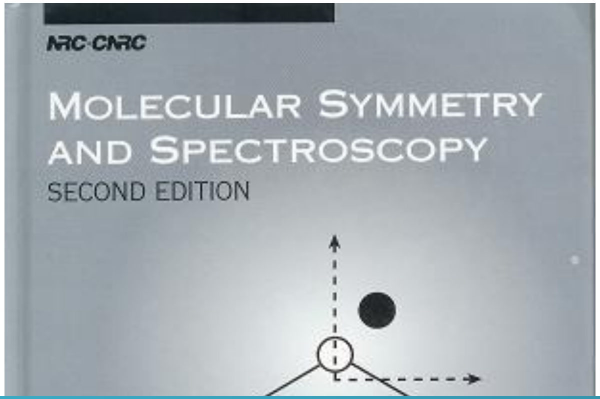
Half-life as function of *J*



and now for something completely different...



The prequel to



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http://bookmark.iop.org/bookpge.htm?&isbn=0750309415

(or see our homepages)