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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-91-J-4130

R&T Code 4131063

Investigation of the role of vibrational excitation in unimolecular reactions

Dr. Deanne Snavely

Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

June 3, 1994

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R&T Number: 4131063

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Contract/Grant Title: Investigation of the role of vibrational excitation in unimolecular reactions

Principal Investigator: Dr. Deanne Snavely

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- a. Number of papers submitted to refereed journals, but not published: 1
- b. * Number of papers published in refereed journals (for each, provide a complete citation): 1
- c. Number of books or chapters submitted, but not yet published: 0
- d. * Number of books or chapters published (for each, provide a complete citation): 0
- e. * Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 2
- f. Number of patents filed: 0
- g. * Number of patents granted (for each, provide a complete citation): 0
- h. * Number of invited presentations (for each, provide a complete citation): 1
- i. * Number of submitted presentations (for each, provide a complete citation): 2
- j. * Honors/Awards/Prizes for contract/grant employees (list attached): 2

(This might include Scientific Society Awards/Offices, Selection as Editors,
Promotions, Faculty Awards/Offices, etc.)

- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:

Graduate Students: 2

Post-Doctoral Associates: 1

including the number of,

Female Graduate Students: 1

Female Post-Doctoral Associates: 0

the number of

Minority Graduate Students: 0

Minority Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students:

Asian Post-Doctoral Associates:

- l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PUBLICATION/PATENTS/PRESENTATIONS/HONORS REPORT continued

a. Papers submitted to refereed journals

"Vibrational Overtone Spectroscopy of Pyridine and Related Compounds", Deanne Snaveley and Joyce Overly, submitted to Journal of Physical Chemistry

b. Papers published in refereed journals

"Vibrational overtone spectroscopy of gaseous metallocenes", Todd Van Marter, Carl Olsen and D.L. Snaveley, Journal of Physical Chemistry, June 1994, in press.

e. Printed technical reports and non-refereed papers

Technical Report No. 14 - "Vibrational overtone spectroscopy of pyridine and related compounds", D. L. Snaveley and Joyce A. Overly

Technical Report No. 15 - "Vibrational overtone activation of methylcyclopropene", Geoff Snaveley, Salah Hassoon and D.L. Snaveley

h. Invited talks at workshops or professional society meetings

"Vibrational coupling in energized molecules: Spectroscopy and kinetics", Photochemical Sciences Colloquium: Diversity in Research, Bowling Green State University, October 1993.

i. Presentations at workshops or professional society meetings

"Hot bands in overtone absorption transitions: High temperature photoacoustic spectra", S Hassoon and D.L. Snaveley, Forty-eighth Symposium on Molecular Spectroscopy, June 1993, Columbus, Ohio.

"Hot bands in overtone absorption of pyrrole, methyl isocyanide and isobutane. Photoacoustic spectra at 140 C", S. Hassoon and D.L. Snaveley, Gordon Research Conference, Molecular Energy Transfer, New Hampton School, New Hampton, New Hampshire, June 20-25, 1993.

j. Honors/Awards/Prizes for contract/grant employees

Member of Review Panel for Research Experiences for Undergraduates in Chemistry, National Science Foundation, November 1993

Member of judging panel for Rao Prize at 48th International Symposium in Molecular Spectroscopy, June 1993

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
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Part II

a. Principal Investigator - Dr. Deanne Snavely

b. Current telephone number - 419-372-2664

c. Cognizant ONR Scientific Officer - Dr. Parbury Schmidt

d. Brief description of project

Our overall goal is to investigate the nature of vibrationally energized molecules. Laser vibrational overtone activation produces energized molecules with specific vibrational excitation which undergo subsequent reaction. In these experiments the total pressure, excitation wavelength and collider gas are varied to determine the specific rate coefficient and collisional deactivation rate constants. Vibrational overtone spectroscopy of nonreactive molecules provides evidence of vibrational energy transfer pathways in reactive systems.

Vibrational Coupling in Reactive Systems

Vibrational overtone excitation creates a narrow distribution of activated molecules compared to other forms of activation. This unique characteristic has allowed us to investigate the energy dependent reaction rate constant and the attributes of the collisional deactivation distribution in gaseous reactions. We have used laser vibrational overtone activation to activate gaseous methyl isocyanide with specific amounts of vibrational excitation. We have determined the experimental specific rate coefficients for this reaction and compared them to the values predicted by RRKM theory.

Using the techniques carefully developed for interpreting the methyl isocyanide reaction we are observing the competition of three unimolecular reaction channels in the ring opening of 1-methylcyclopropene.

Vibrational Coupling in Nonreactive Systems

Internal vibrational state coupling is observed in the vibrational spectrum. Analysis of the complete vibrational overtone spectrum elucidates the different coupling mechanisms in highly energized molecules. It is clear from our spectra that the off diagonal anharmonicities dominate the vibrational behavior at high energy. We record the extremely weak near infrared (using Fourier transform spectroscopy with a 20 m cell) and visible absorption spectra (using laser intracavity photoacoustic absorption spectroscopy) of related nonreactive molecules in order to identify and quantify these anharmonicities.

e. Significant results during last year.

High vibrational overtone spectroscopy of heteroaromatics

In the previous year we demonstrated that the NH overtone spectrum of pyrrole was unusual in that multiple absorptions appeared where only one local mode band should have appeared. Our current investigation of the CH vibrational spectrum of pyrrole and other heteroaromatic compounds

tests the description of the overtone spectra and vibrational coupling at high internal energies. The spectrum of benzene, which displays one broad absorption at each quantum level, has long been used as the paradigm for the behavior of an energized system of equivalent oscillators and intramolecular vibrational redistribution. As opposed to benzene, our spectra of gaseous pyridine, 3-fluoropyridine, 2,6-difluoropyridine and pyrazole all possess two vibrational bands at each quantum level. From a comparison of the transition wavenumbers, widths and relative intensities of the absorptions in these spectra we have developed a model which relates these spectra to that of benzene. A simulation of the pyridine spectrum is underway.

Hot Band Absorptions in Local Mode Spectra

We have gained significant new insight into vibrational overtone coupling by discovering that one of the major absorptions in the $\nu=4$ NH stretch spectrum of pyrrole is a hot band arising from the NH wagging normal mode. This surprising fact was identified by observing the temperature dependence of the relative intensities of the overtone bands. These hot band transitions often overlap the principal local mode absorption, broadening the overall band. Local modes possess diagonal anharmonicities, typically -50 to -80 cm^{-1} . We have documented large anharmonicities, -20 to -25 cm^{-1} , for these hot band absorptions in the visible. We have discovered a new hot band in dimethylamine which is similar to the hot band in pyrrole. It borrows absorption strength from the principal NH stretch transition.

Vibrational Overtone Activation of Methylcyclopropene

Laser vibrational overtone activation was used to investigate the reaction channel competition in the isomerization of a new 95% pure sample of 1-methylcyclopropene. The vibrational overtone activation of three types of CH stretches (methyl, methylenic and olefinic) in the $6\nu_{\text{CH}}$ transition was initiated and all three products (2-butyne, 1,3-butadiene and 1,2-butadiene) were detected by gas chromatography. We have derived a method for constructing the Stern-Volmer plots for the appearance of each individual product. The product yield ratios were compared to the RRKM ratios which correspond to the low pressure limit. The product yield ratio for the methylenic photolysis compared well with the RRKM ratio but the olefinic product yield was approximately 40% lower than the RRKM ratio. Contrary to the predictions of kinetic theory, the product ratios of 1,3-butadiene to 2-butyne were independent of pressure. The master equation simulations are underway to interpret these results.

Vibrational Coupling in Activated Hydrocarbon Metal Complexes: Vibrational Overtone

We have observed vibrational mixing in the visible vibrational absorption spectrum in Π bonded organometallic complexes. These Π bonded complexes are widely used in catalysis and organometallic chemistry. These changes in the vibrational spectrum document the effect on the ligand when a metal bonds to the Π cloud. In ferrocene, acetylferrocene, ruthenocene and cyclopentadienyltitaniumtrichloride the third overtone of the olefinic C-H stretch in gaseous

cyclopentadiene mixes with other modes, principally the CC stretch and the CCH bend, in the presence of the metal. We have now demonstrated the same effect in a Π bonded benzene complex, benzene chromium tricarbonyl.

g. Brief summary of plans for next year.

Reactive Systems The theoretical description of the product yield ratios for the reaction of 1-methylcyclopropene will occupy a major portion of next years effort. I have hired a theoretical chemist, Dr. Igor Ouporov, to proceed with the master equation simulations of our experimental data. In addition we plan to photolyze 1-methylcyclopropene in argon at the fourth and fifth overtones in order to test our hypothesis regarding collisional deactivation in this system.

Nonreactive systems

Work on identifying and characterizing vibrational overtone hot bands will continue. We want to know how hot band absorptions change with increasing quantum number and why are the anharmonicities and intensities so large. Our development of a method to routinely record intracavity spectra at higher temperatures will allow us to explore this area, especially in gaseous amines.

Our discovery that the overtone spectrum of cyclopentadienyl changes when it complexes to a metal will be pursued. Further study of these changes is aimed at characterizing the vibrational coupling involved in activating hydrocarbons with metal centers. We are studying the spectrum of dichloro-1,5-cyclooctadiene palladium (II) and benzene chromium tricarbonyl. We have begun the synthesis of cyclobutadiene iron tricarbonyl.

g. Names of graduate students and post-doctorals currently working in the laboratory

Dr. Salah Hassoon - Post-doctoral

Joyce Overly - graduate student

Andre Fedorov - graduate student

Oleg Grinevich - graduate student

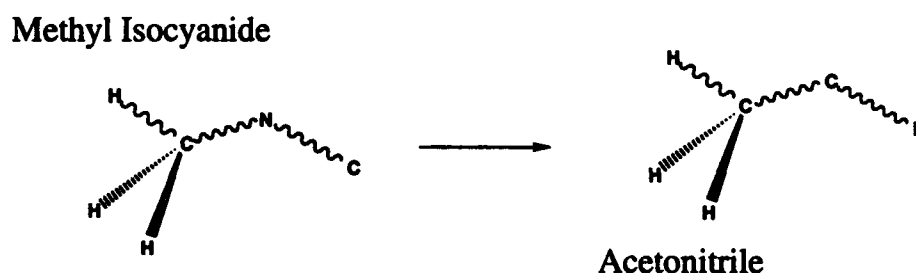
Geoff Snavely - MS in Chemistry, 1993

Hot Bands and RRKM Theory: Specific Vibrational Overtone Excitation in the Isomerization of Methylisocyanide: Reaction Kinetics meets Overtone Spectroscopy

Vibrational overtone spectra of gaseous hydrocarbon samples typically exhibit band contours which are broad and unstructured. Both homogeneous (which derives from the coupling of the bright state to the nearly isoenergetic states - intramolecular vibrational relaxation) and inhomogeneous (arising from the multitude of rotational-vibrational transitions from thermally populated states) broadening contribute to these large widths. Discerning the consequences of these two broadening mechanisms is critical to the search for mode selective chemistry.

We have identified vibrational hot bands from their temperature dependence in the visible vibrational overtone spectra of several gaseous molecular samples. Vibrational hot bands are absorptions which originate from molecules with one or more quanta in the low frequency vibrational modes of the molecule (Vu-graph 1). These hot bands borrow intensity from the main allowed transition and are observed to the red of the principal band. This "red shift" is large being up to 100 cm^{-1} at $v=4$ in some cases. Using the Boltzmann expression for the relative intensities of the hot band and its principal band, the identity of the low frequency mode is determined.

In view of the appearance of hot bands, the interpretation of the experimental specific rate coefficients determined in vibrational overtone activation must be reconsidered. These specific rate coefficients have been determined for the isomerization of methyl isocyanide to form acetonitrile



for photolysis wavelengths across the $5\nu_{\text{CH}}$ and $6\nu_{\text{CH}}$ band contours according to the following Stern-Volmer type equation.

$$k_{\text{app}}^{-1} = k_a^{-1} + k_d k(E)^{-1} k_a^{-1} [M]$$

k_{app} is the product yield divided by the photolysis time and the photolysis laser power

k_a is the rate constant for the photoactivation

k_d is the collisional deactivation rate constant

$k(E)$ is the specific rate coefficient

$[M]$ is the total pressure in the photolysis cell

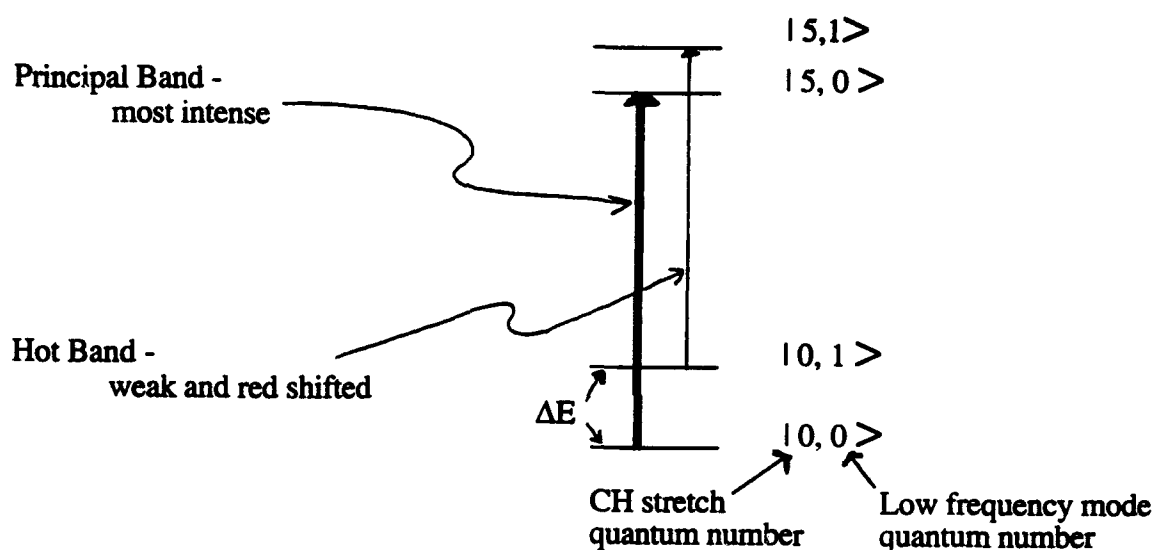
The measured specific rate coefficients at seven different wavelengths across the band contours of the $5\nu_{C-H}$ and $6\nu_{C-H}$ transitions increased monotonically with increasing photolysis energy. These measured rates corresponded exactly to the calculated specific rate coefficients. The RRKM rate curve was calculated using the Gilbert program.

Focusing in on the $5\nu_{CH}$ band contour (Vu-graph 3) we see that the photolysis at 13605 cm^{-1} excited a hot band transition. From the dependence of the intensity on temperature, the ΔE indicates that this transition originates from states with one quantum of excitation in the CNC bend. Consequently, molecules excited at 13605 cm^{-1} possess more internal energy than those photolyzed at higher wavenumbers. Using the bending energy plus the photon energy, molecules photolysed at 13605 cm^{-1} would possess about 100 cm^{-1} more internal energy than those photolysed at the peak maximum, 13763 cm^{-1} . Given the experimental error in our rate coefficients we would have been able to measure this difference in the rates and should have observed a nonmonotonic increase with increasing photolysis energy.

This leaves us with a contradiction between the kinetic and spectroscopic evidence for this reaction. An explanation of our kinetic results could be that we see hot band temperature dependence in the red side of the $5\nu_{CH}$ transition but it is possible that there are other vibrational transitions contributing to the overall red side intensity. Perhaps at the one photolysis wavenumber chosen on the red side of the $5\nu_{C-H}$, we were photolyzing a combination band rather than a hot band transition. This would explain our monotonic increase in the specific rate coefficient with increasing energy. On the other hand it may be that the photolysis at 13605 cm^{-1} placed energy within the molecule in such a way as to retard the progress toward reaction. We will pursue this fundamental question further

Vibrational Overtone Hot Bands and RRKM Theory: Specific Vibrational Activation in the Isomerization of Methyl Isocyanide

Energy level diagram showing hot band transition



Spectral shift of hot band can be large

$$\text{Red Shift} = X_{ph} \nu_p \nu_h$$

Hot band anharmonicity \rightarrow X_{ph}

Local mode quantum number \rightarrow ν_p

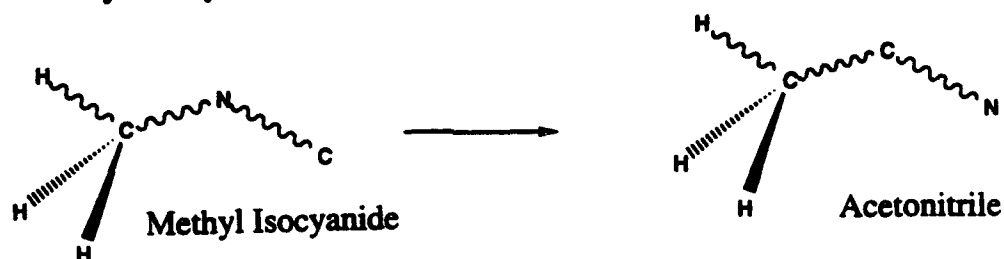
Hot band quantum number \rightarrow ν_h

Hot band intensity based on Boltzmann populations at two different temperatures

$$\frac{\text{Intensity at } T_1}{\text{Intensity at } T_2} = C \exp\{-\Delta E/k(1/T_1 - 1/T_2)\}$$

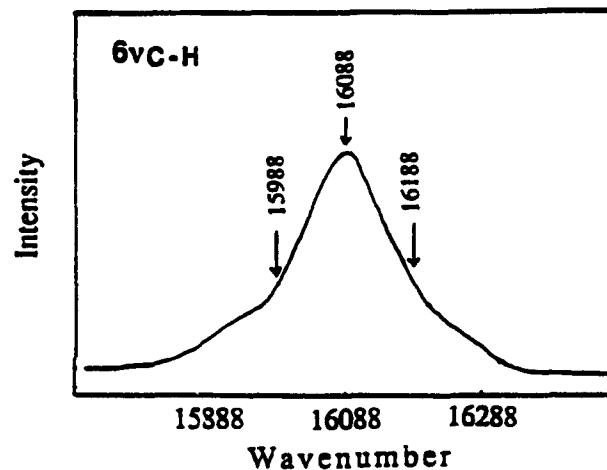
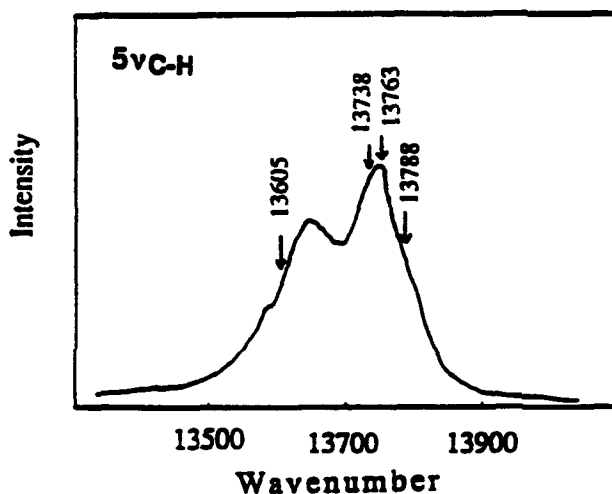
Vu-graph 2

Reaction of methyl isocyanide isomerization to acetonitrile



Specific vibrational overtone activation of gaseous methyl isocyanide

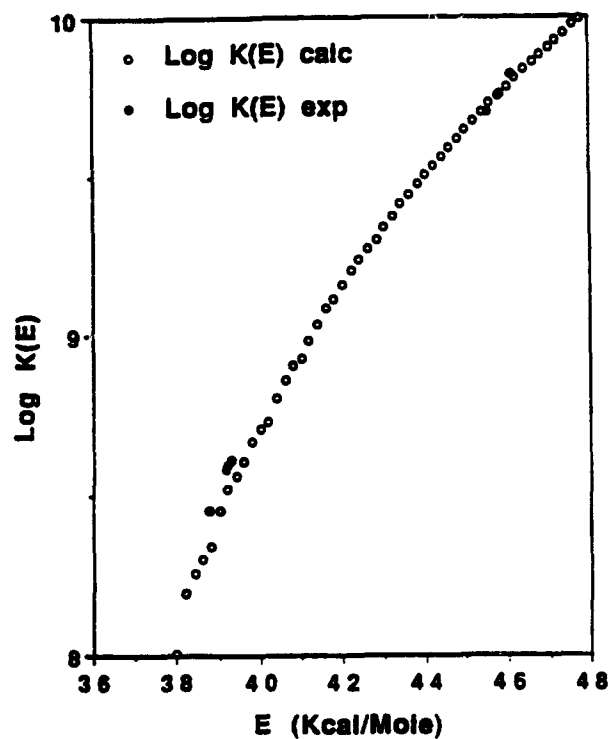
Arrows mark photolysis wavenumbers along band contours



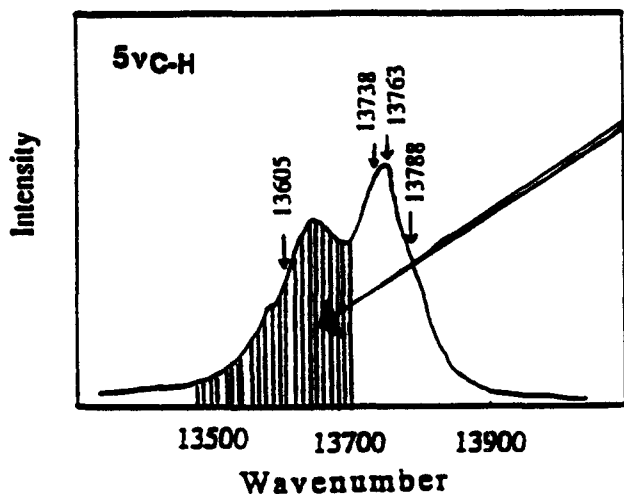
Comparison of experiment and theory

RRKM depends on vibrational states and at higher internal energies is a smooth curve

Experimental K(E) compare well with theory



Temperature dependence of the intensity of the 5_νCH spectrum

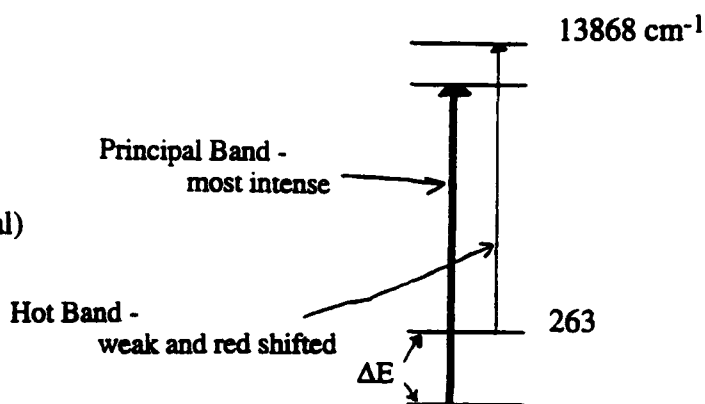


Indicates hot band at 13660 cm⁻¹

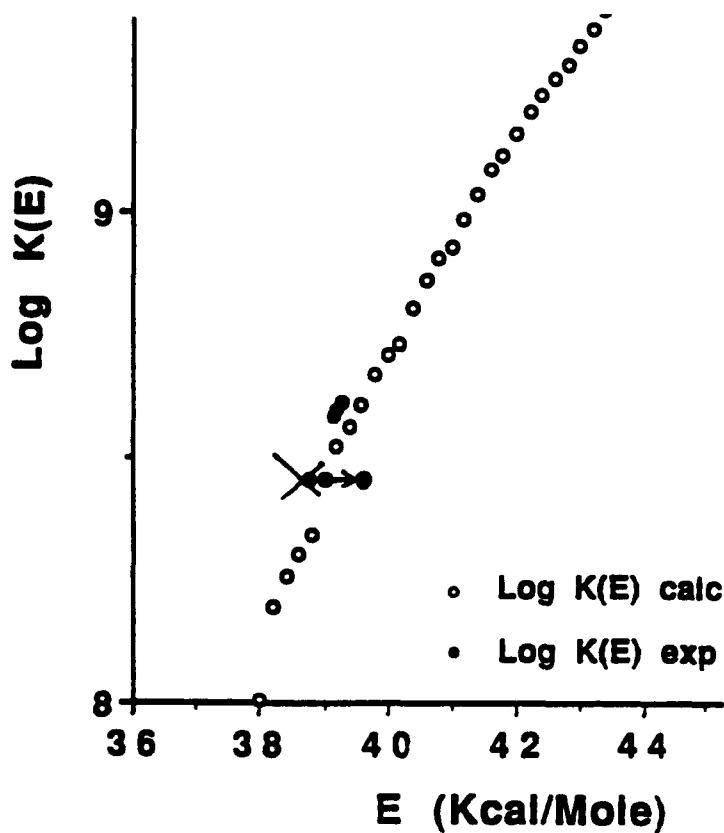
ΔE of 208 cm⁻¹ identifies the thermally populated level as the CNC bending mode

New assignment of this overtone peak

Total internal energy of molecules
 photolyzed at 13605 cm⁻¹ is
 13605 + 263 = 13868 cm⁻¹ (39.6 kcal)



New comparison of experiment to theory shows contradiction in lowest energy



Molecules with excitation in the bending
 vibration react slower than others

This new interpretation must be
 further explored