Nonthermal Chemistry Induced by Visible Light

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NOTE

Metastable Diacetylene Reactions as Routes to Large Hydrocarbons in Titan's Atmosphere

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ICARUS **123,** 578–583 (1996)

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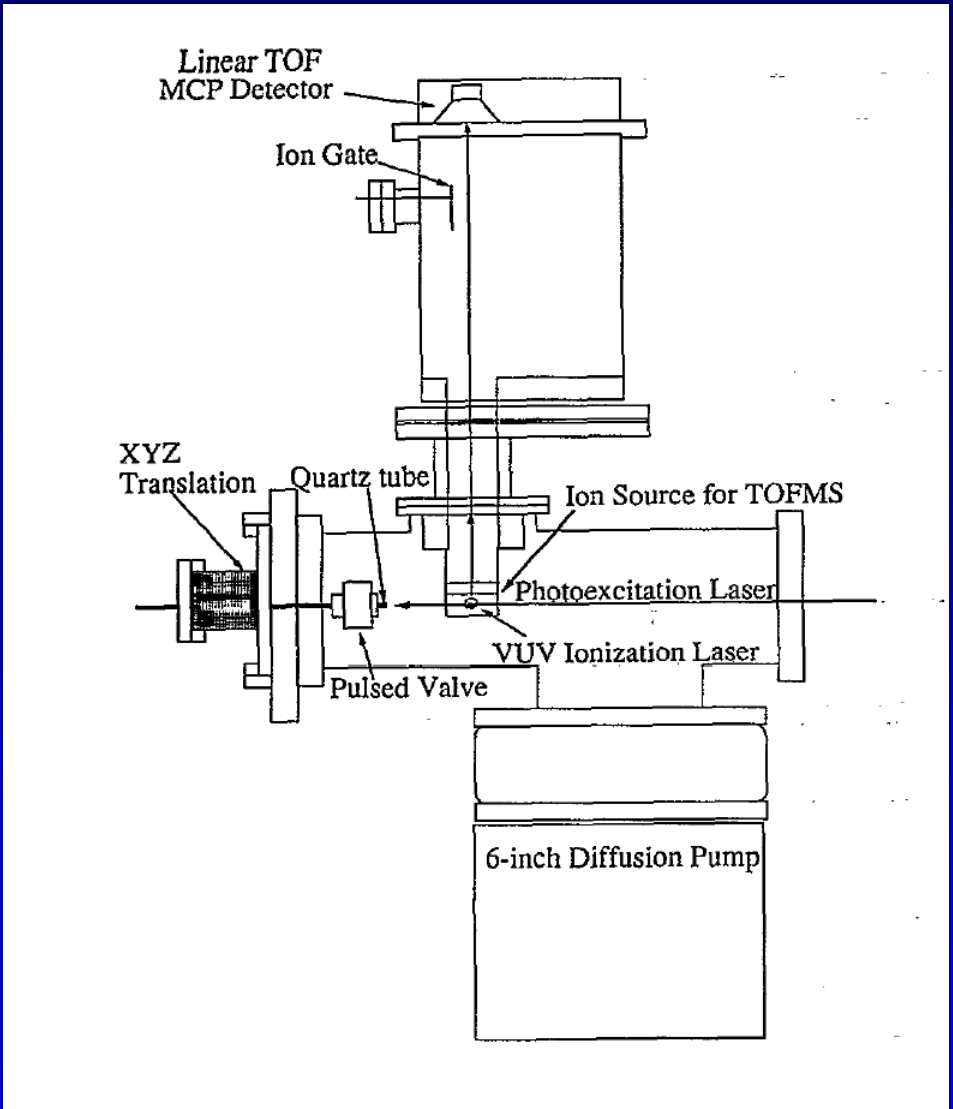
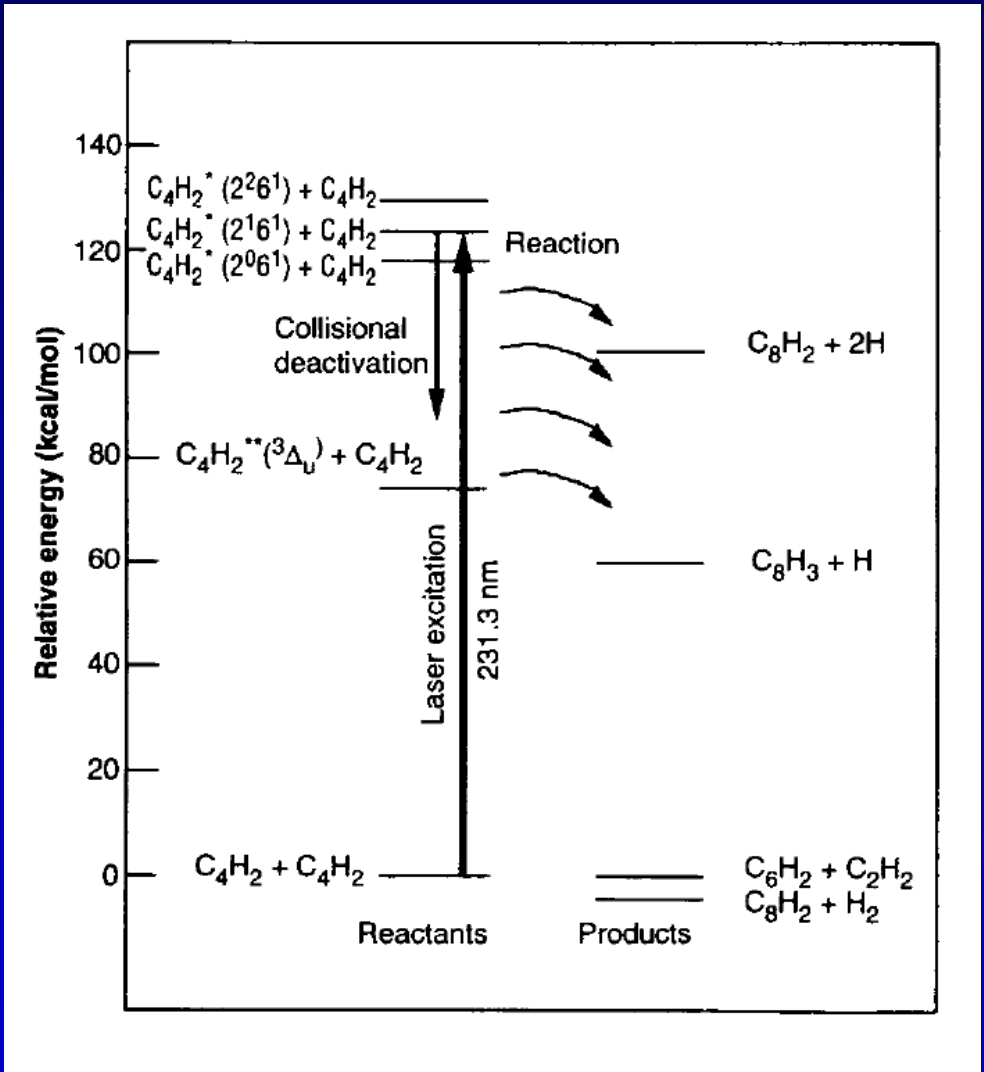
Recent experimental data on the relative rates of metastable diacetylene ($C_4H_2^*$) reactions are used to estimate the potential effects of their inclusion into the photochemical model of the atmosphere of Titan. It is demonstrated that the reactions of $C_4H_2^*$ have the potential for successfully competing with free radical routes to formation of larger hydrocarbon species in Titan's atmosphere, especially at altitudes below about 200 km. At an altitude of 105 km, the net production rate of larger hydrocarbons from $C_4H_2^*$, C_4H, and C_2H is estimated to be in the ratio 90 : 30 : 1.

Reactions of Triplet Diacetylene HCCCCH
Zwier Group, Purdue

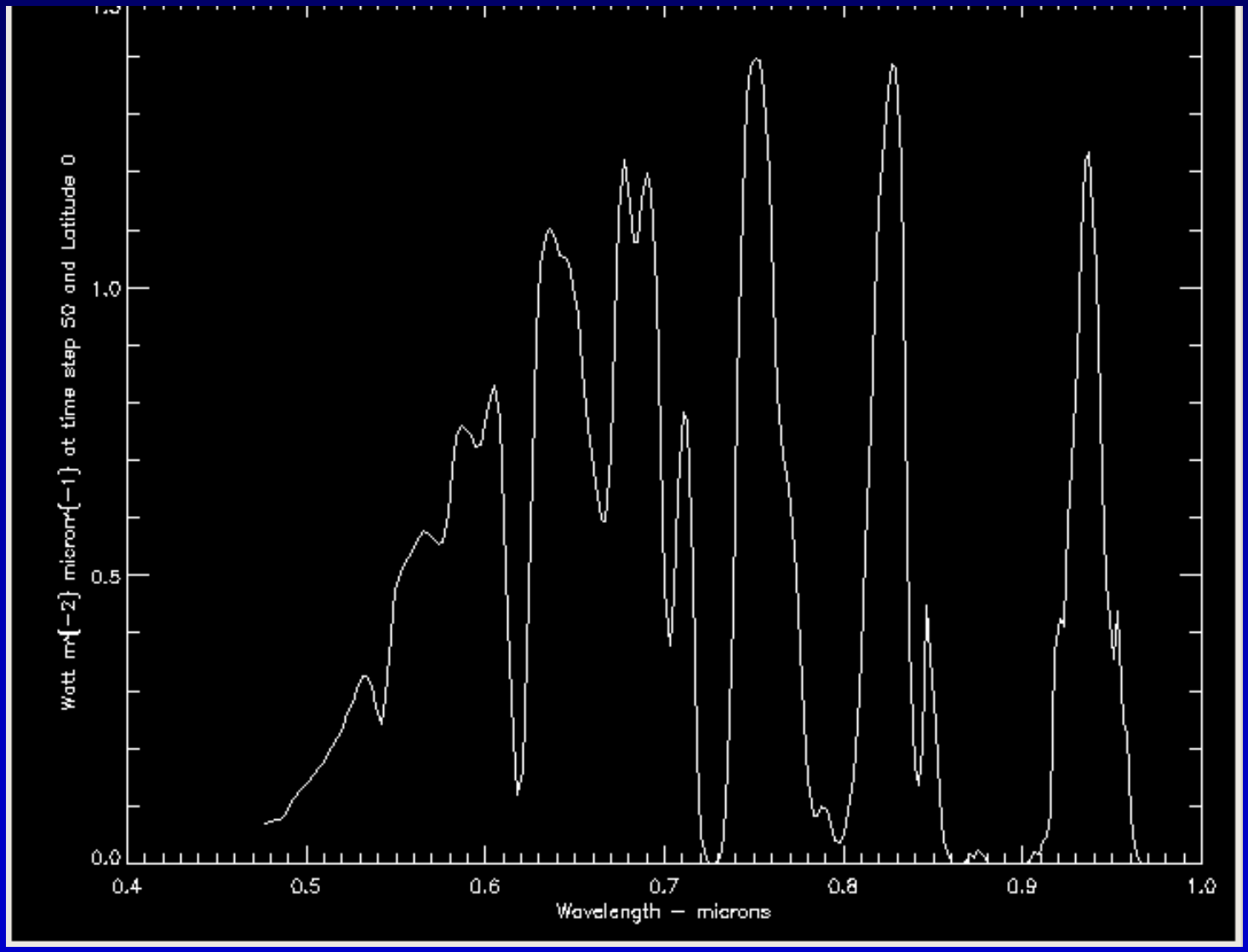


Photoinduced Reactivity of Diacetylene, C_4H_2

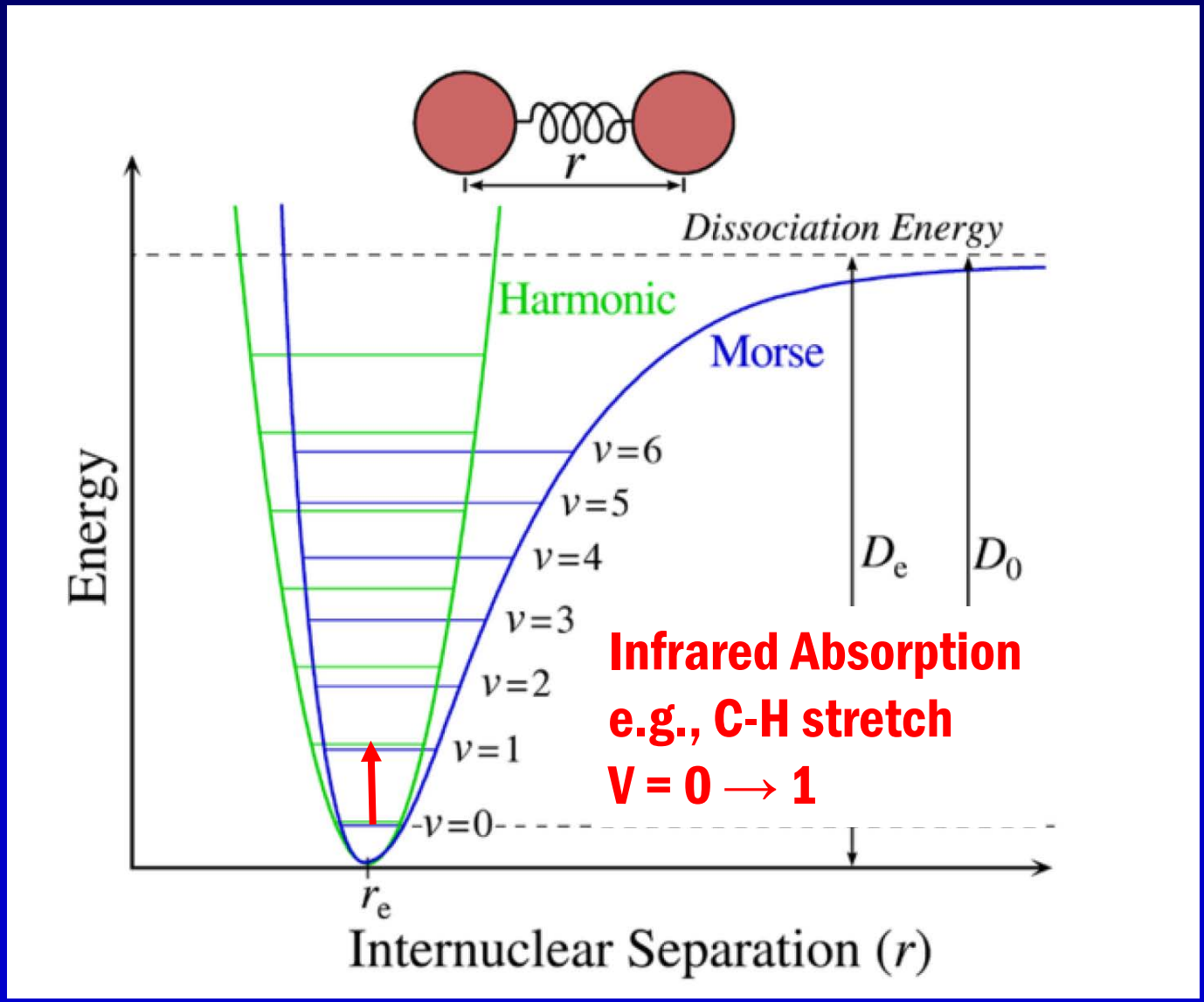


Zwier, Science 258, 1630 (1992)

Spectrum of Solar Radiation on Titan



Vibrational Levels of Molecules



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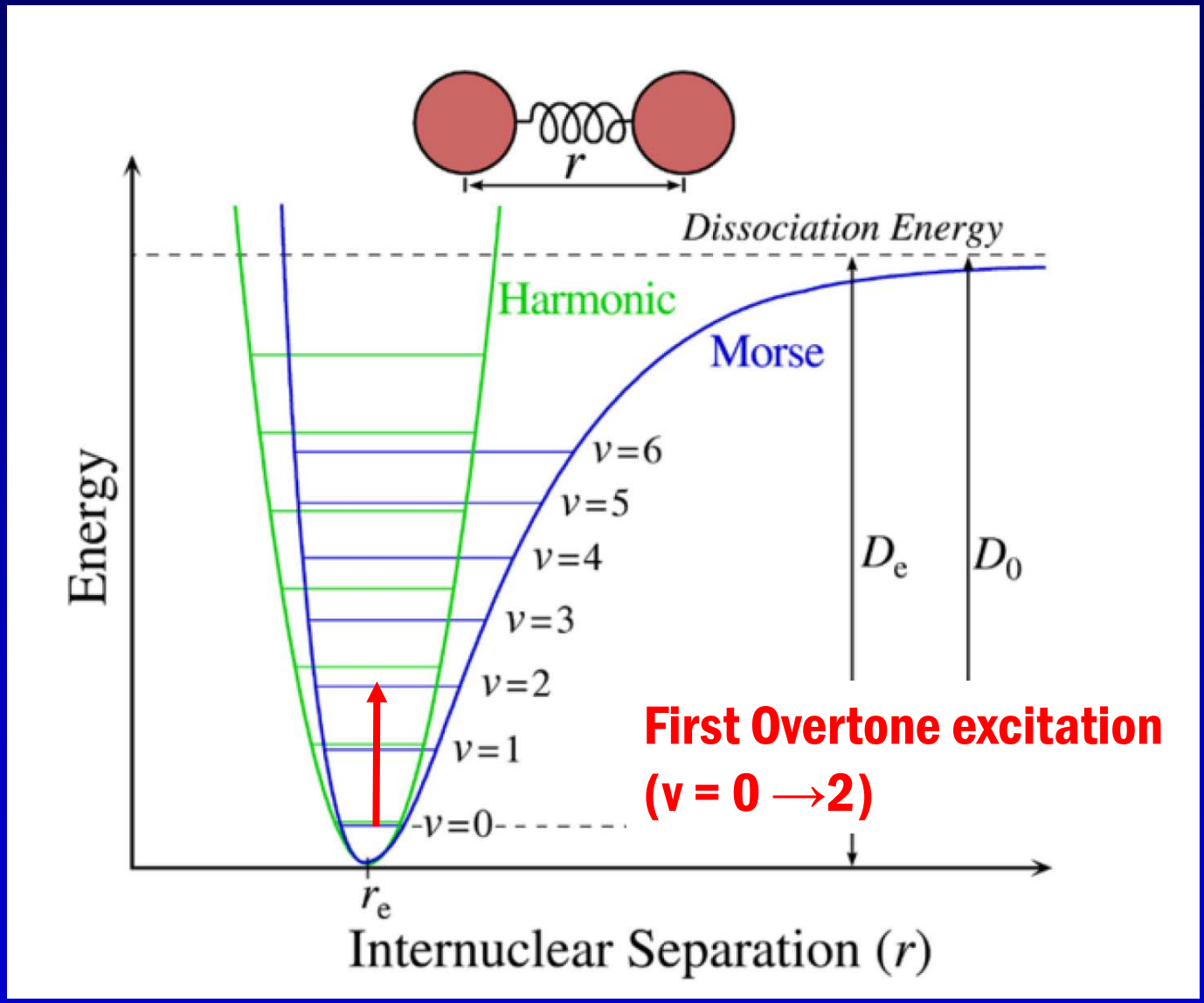
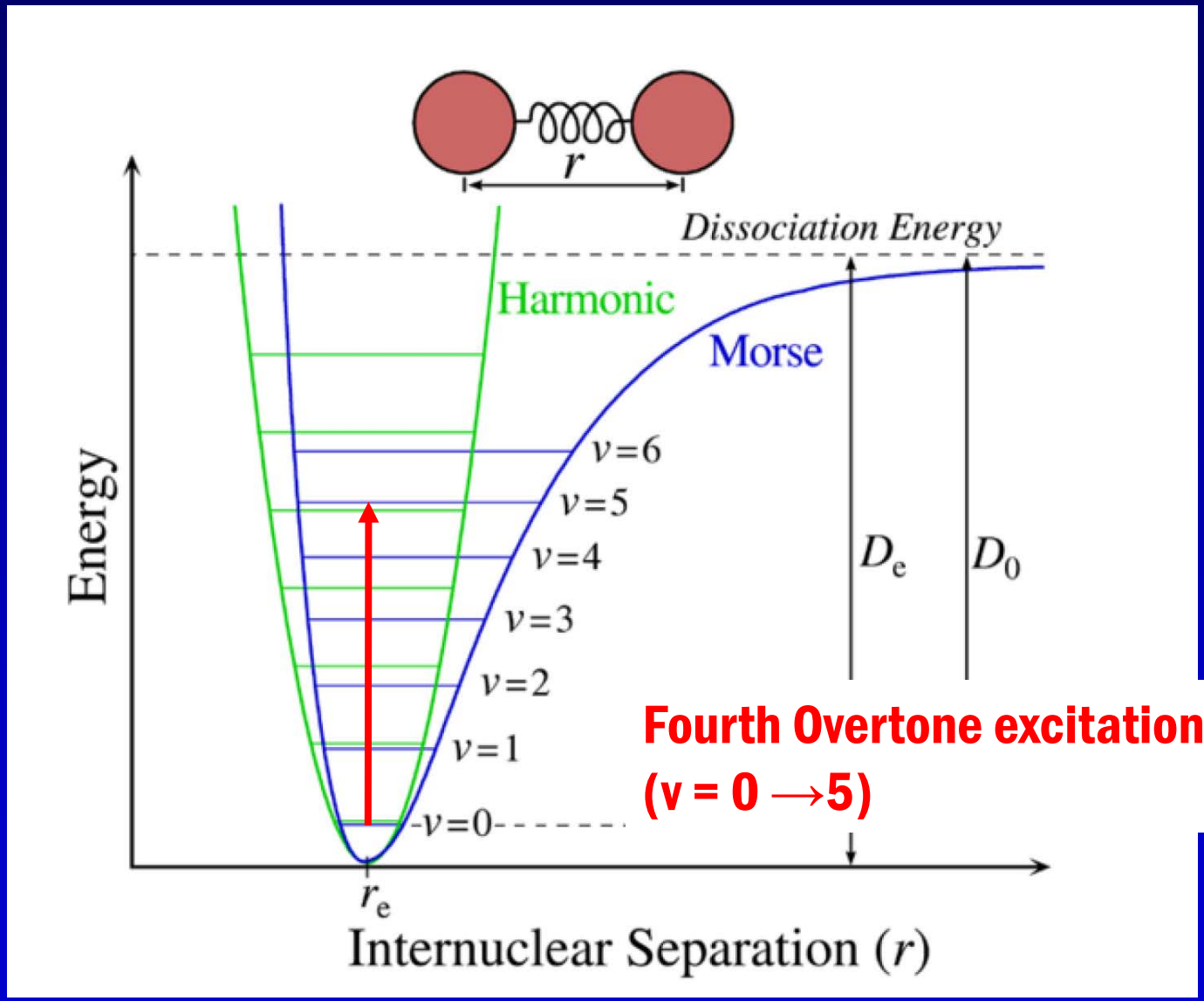
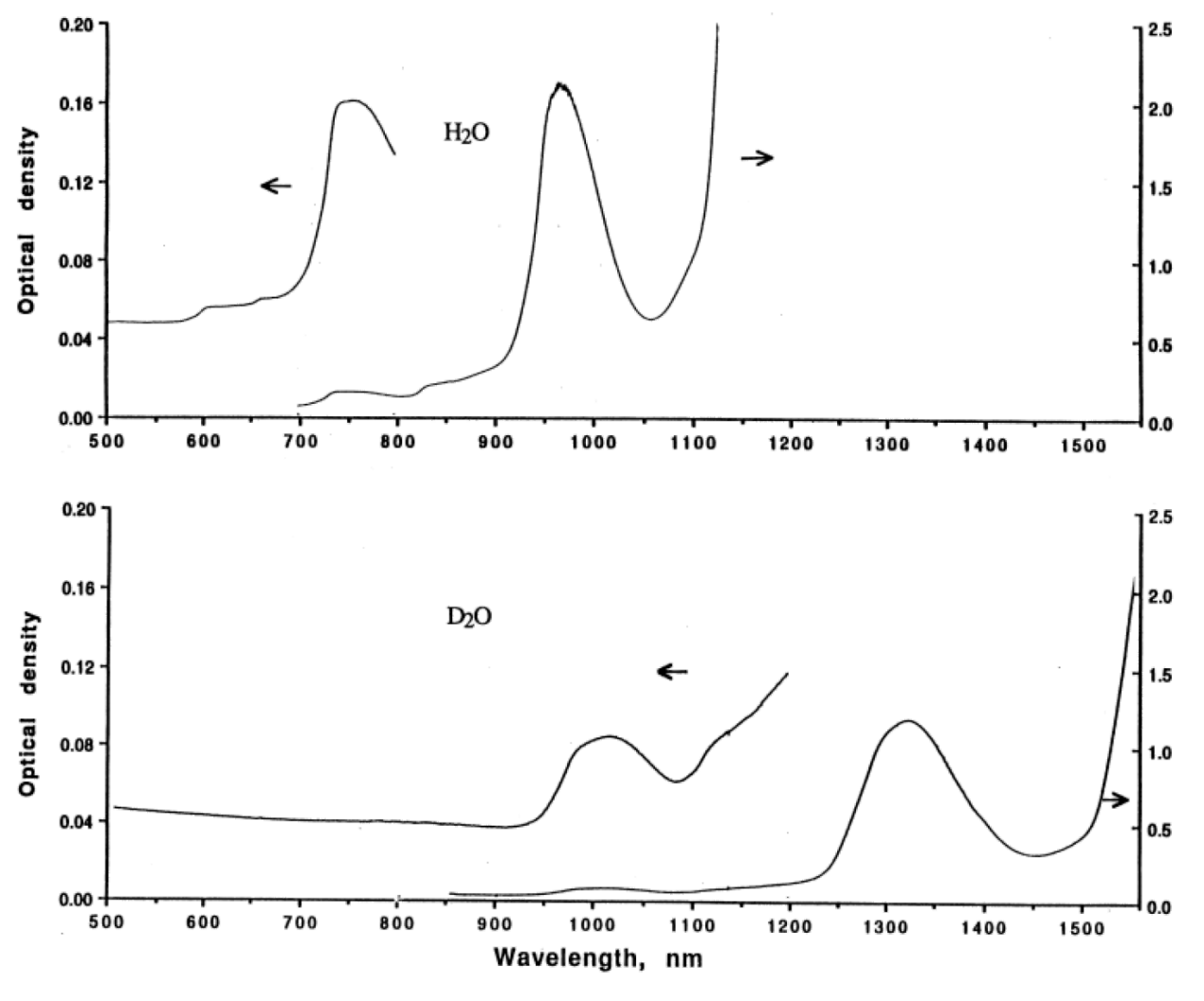


Vibrational Levels of Molecules



Why is the ocean blue?

Due to OH Overtone Absorption of red light



Red sky at night: Long-wavelength photochemistry in the atmosphere

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CHRISTIAN GEORGE
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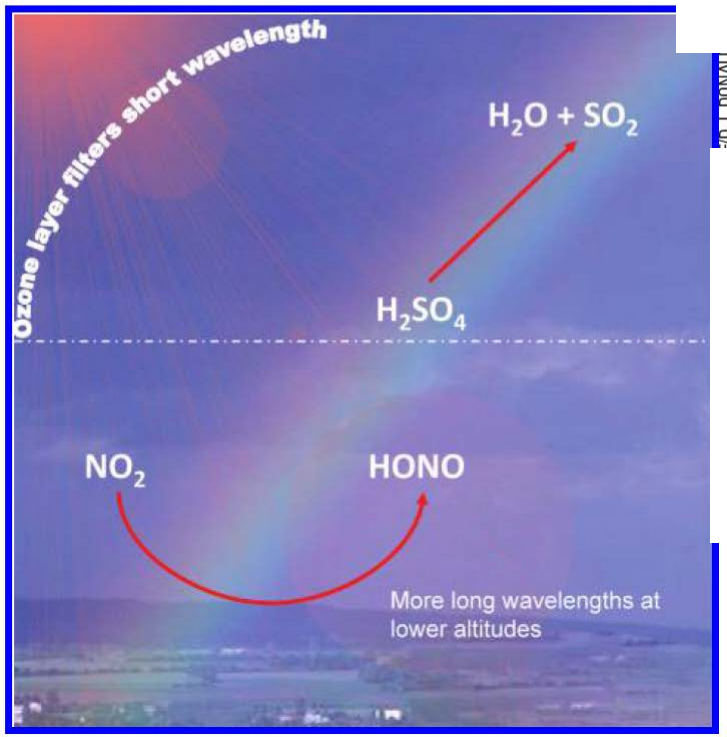
VERONICA VAIDA
University of Colorado, Boulder, Colorado



Chem. Rev. **2003,** *103,* 4717–4729

Atmospheric Photochemistry via Vibrational Overtone Absorption

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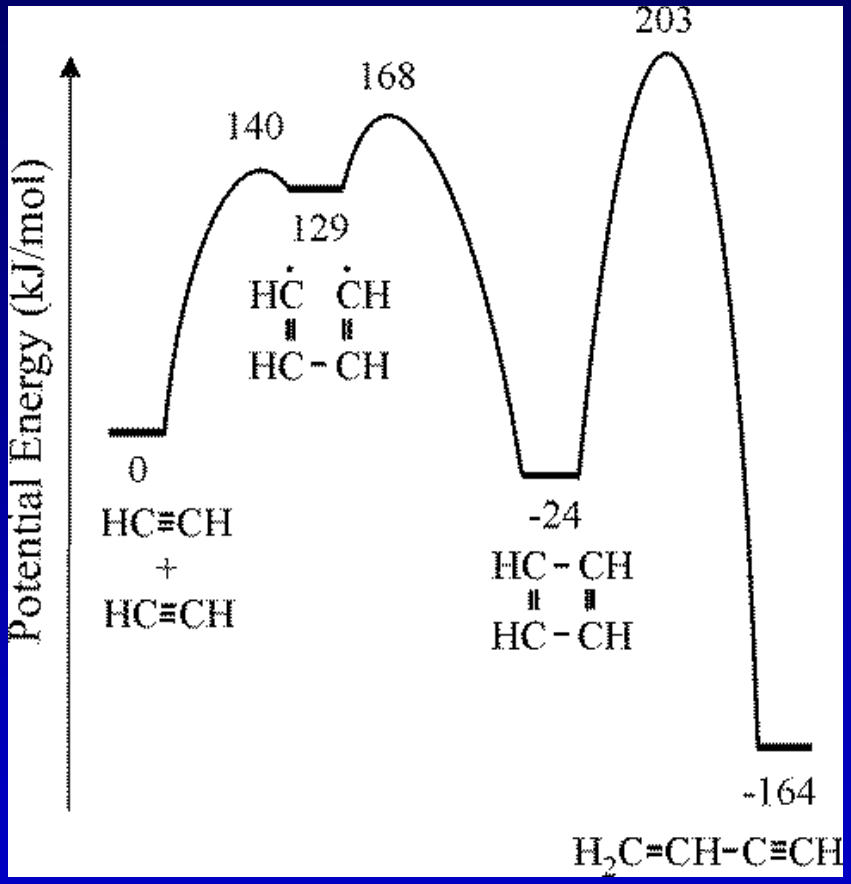
In polyatomic molecules containing O−H, C−H, and N−H groups, the small mass of the hydrogen atom means that X−H stretching frequencies are considerably higher than those of other vibrational modes. This feature and the generally large anharmonicities associated with such X−H stretches, give rise to absorption transitions to higher vibrational levels becoming less "forbidden" (and hence stronger) than for other types of overtone absorption. At

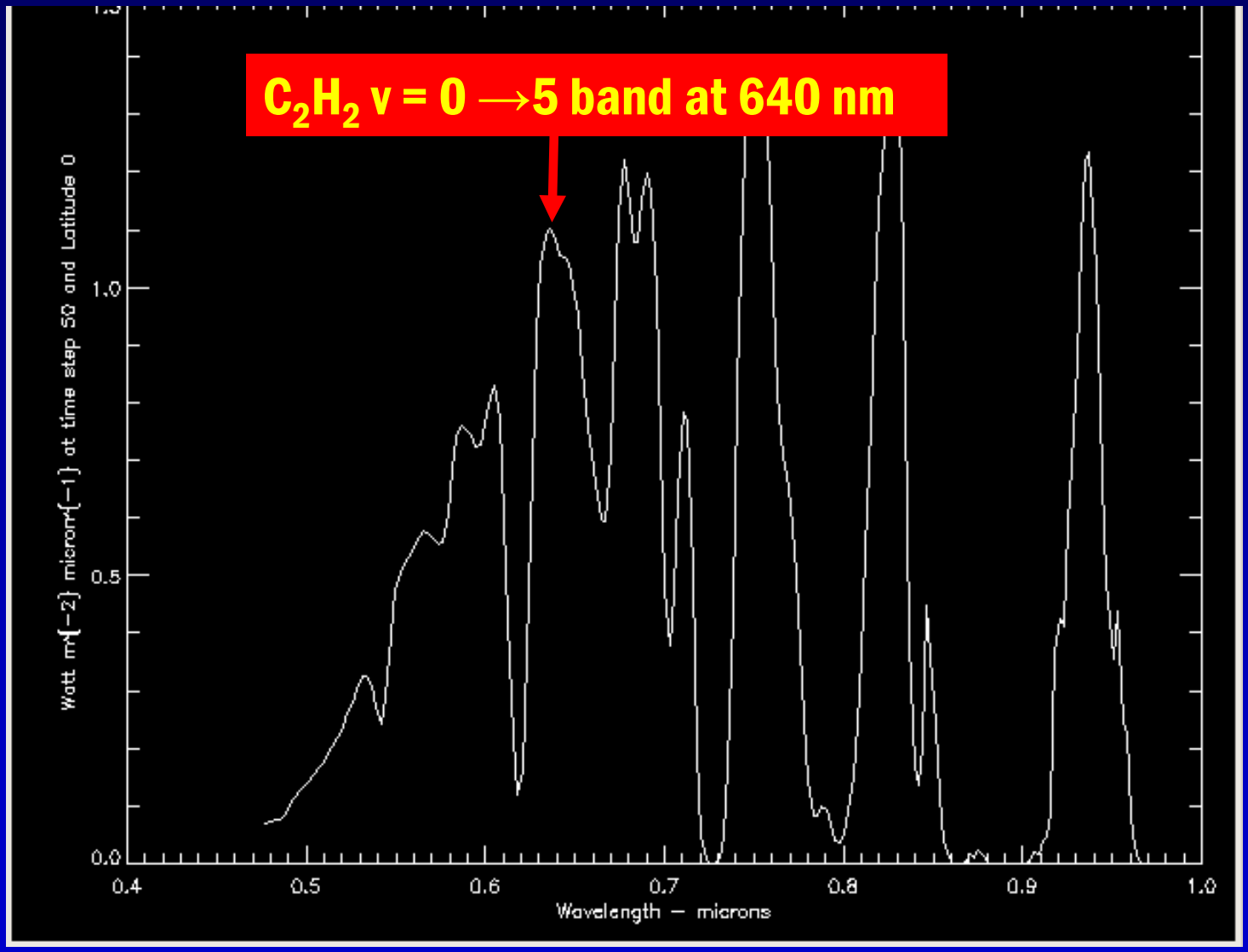
Calculated Singlet C_4H_4 Energetics
Mebel, J. Chem. Phys. 125, 133113 (2006)



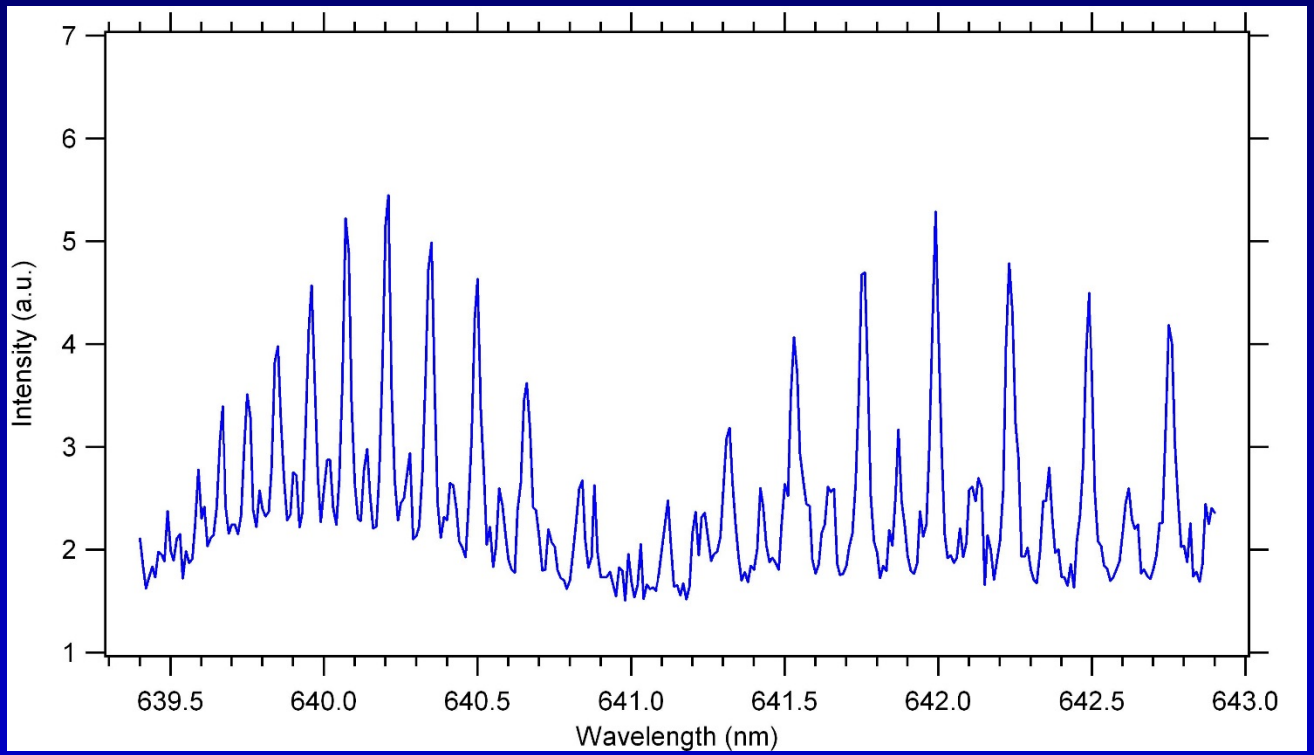
Calculated singlet C_4H_4 energetics (kJ/mol)

Addition barrier is 140 kJ/mol.
Corresponds to photon at 856 nm

Spectrum of Solar Radiation on Titan

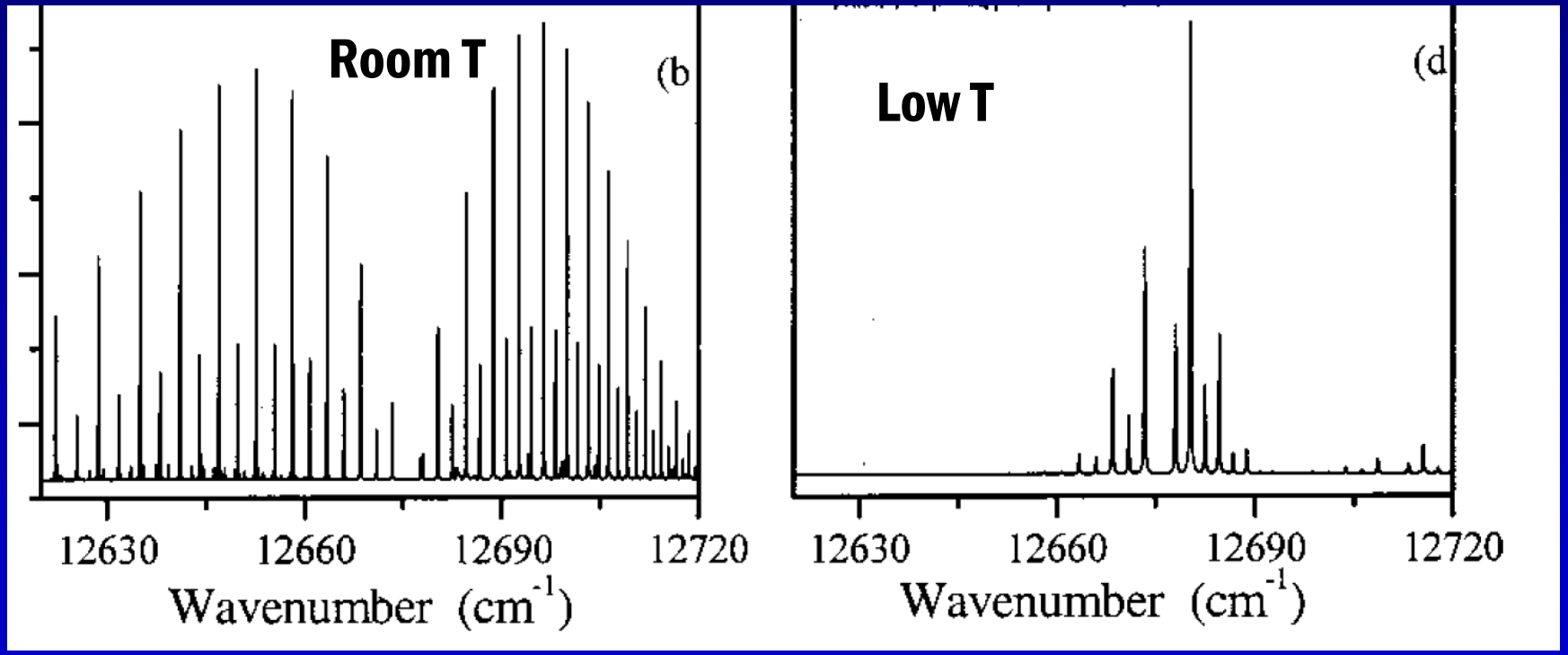


Acetylene 5 ν_{CH} Photoacoustic Spectrum

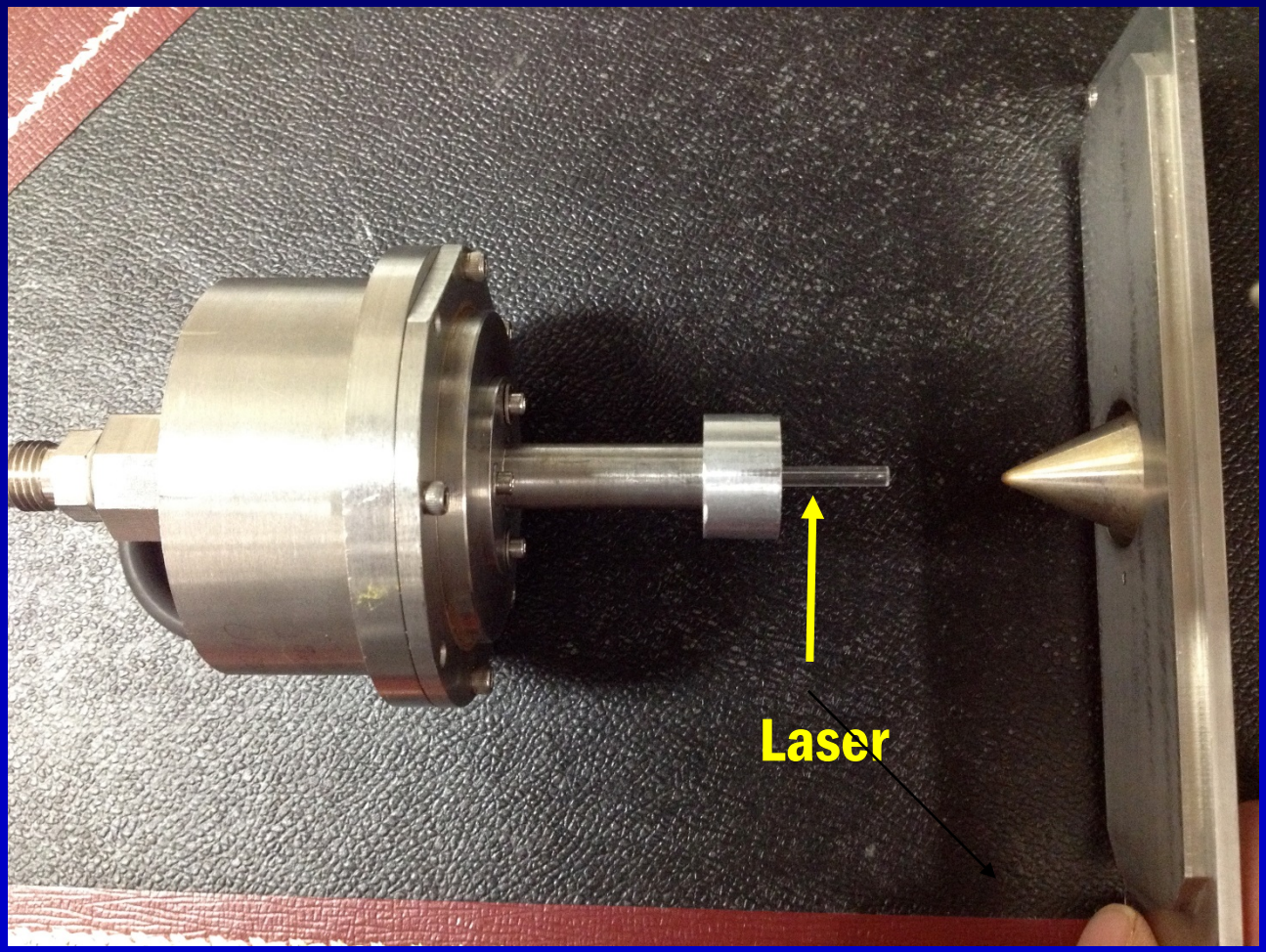


Acetylene 4 v_{CH} Overtone Spectrum (787 nm):

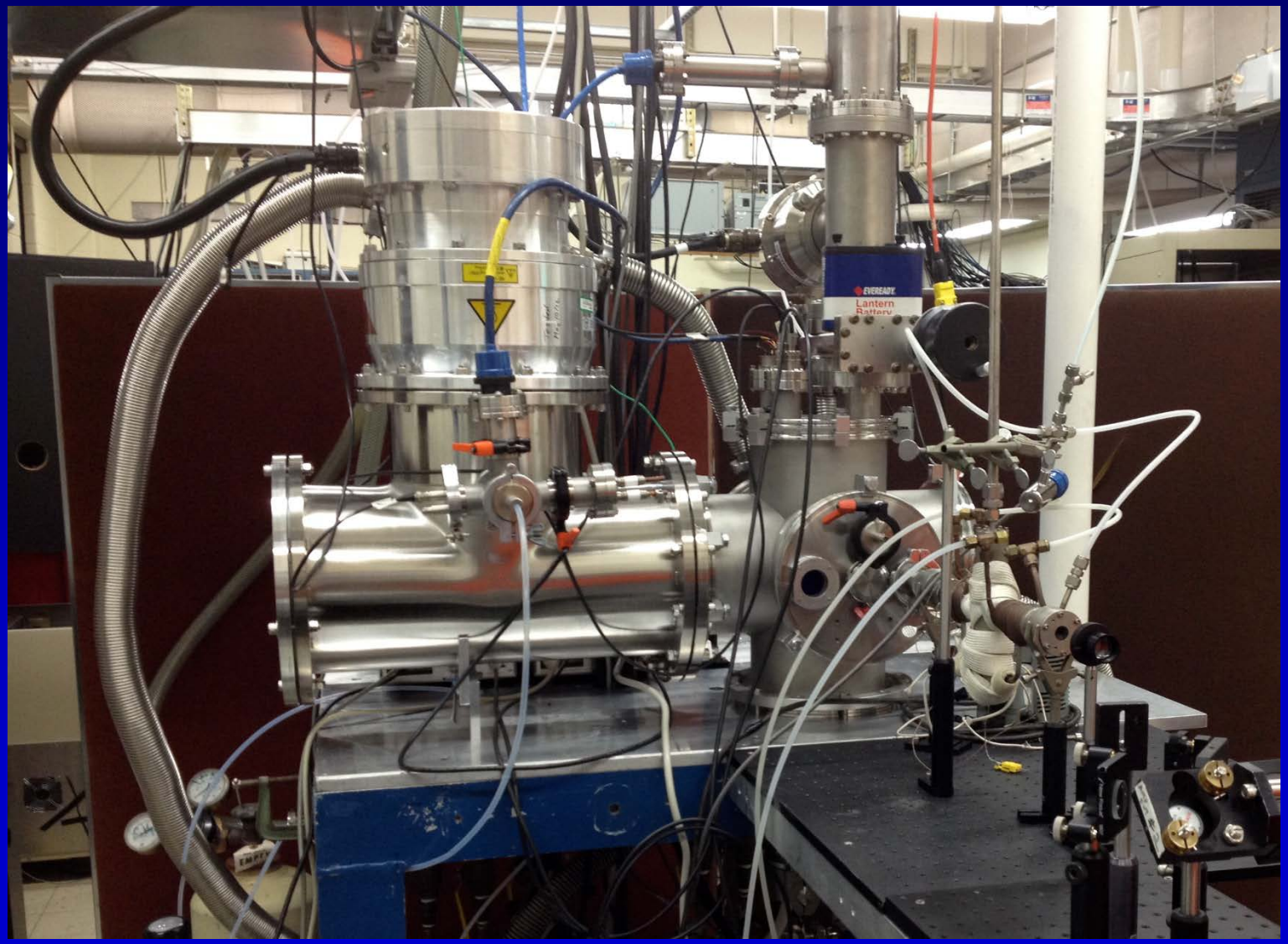
Room Temp vs. Molecular Beam.



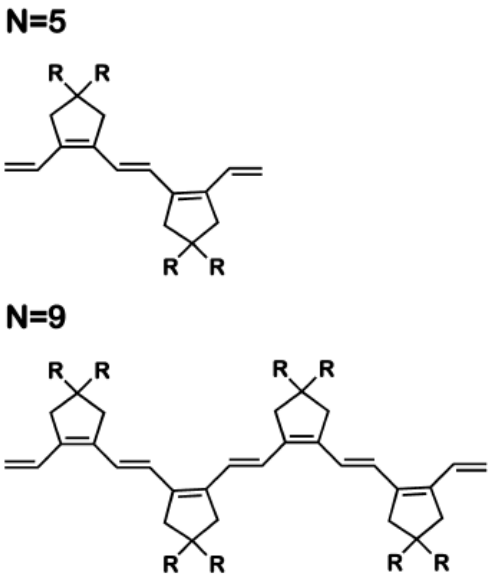
Pulsed Valve/Flow Reactor



VUV Photoionization TOF Apparatus



Absorption Spectra of Polyenes
Christensen, J. Phys. Chem. A 117, 1449 (2013)



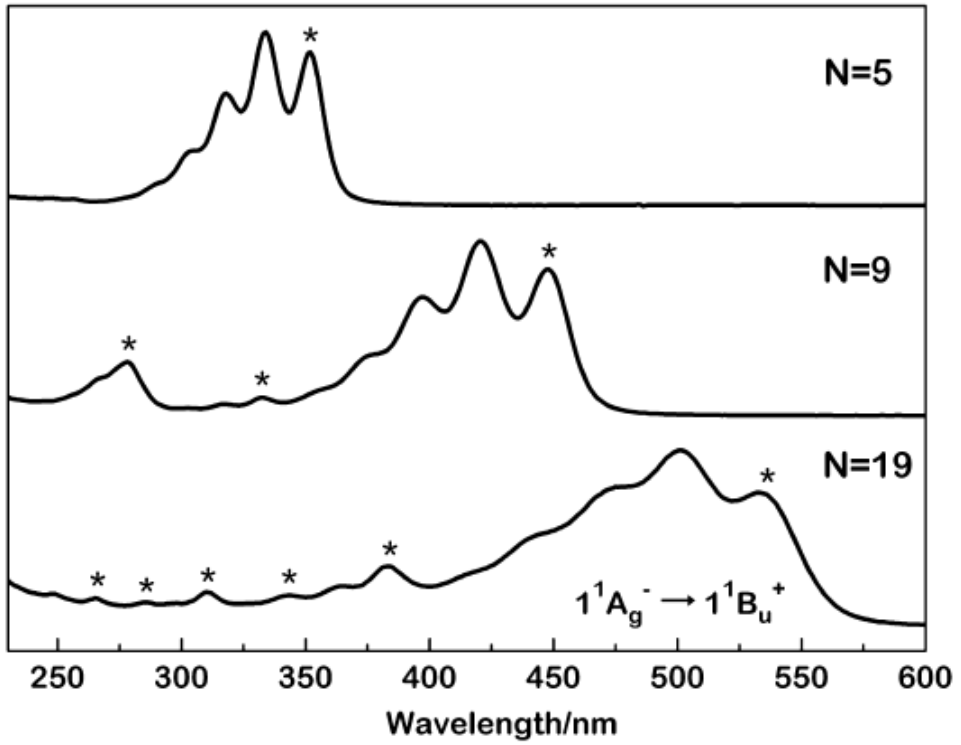


Figure 2. Room temperature, steady-state absorption spectra of $N = 5$, 9, and 19. Asterisks indicate positions of electronic origins ((0–0) bands) for allowed transitions.

Electronic Excitation Energies of Polyenes Decrease with number of monomer units, N "1D particle in a box"

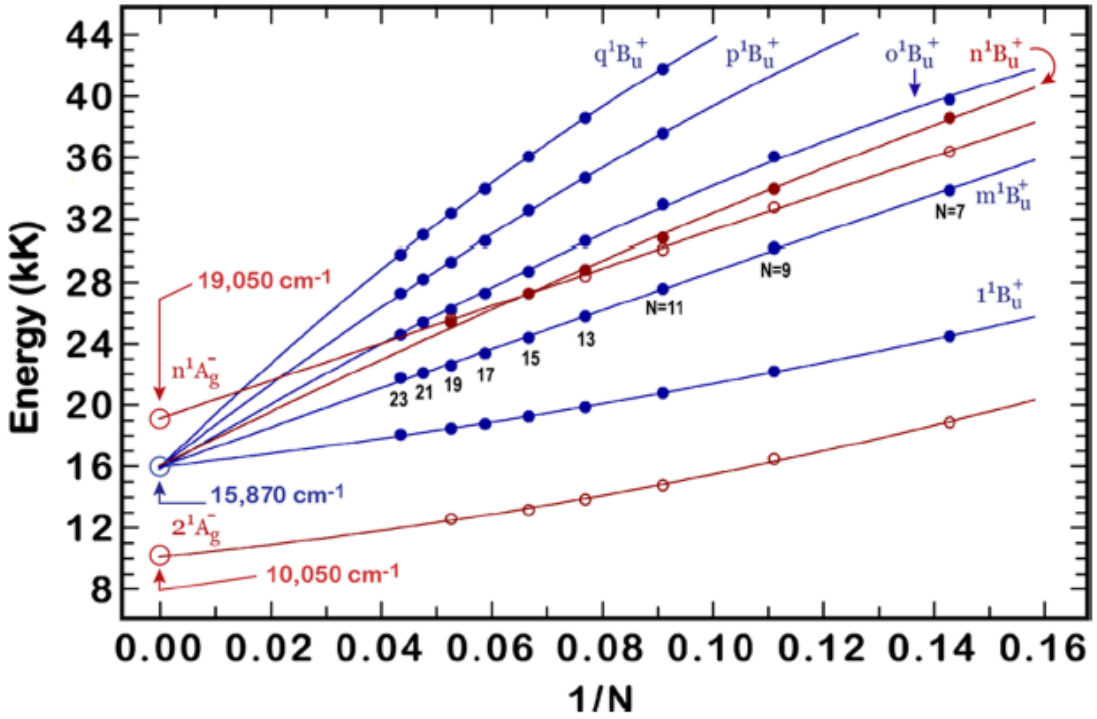


Figure 11. Electronic transition energies of $N = 7-23$ polyenes in room temperature 2-MTHF (data from Table S2, Supporting Information) (1 kK = 10^3 cm^{-1}). Data points and lines in blue correspond to absorption measurements, and data points and lines in red are derived from transient absorption measurements. Open circles designate measurements of $^1A_g^-$ state energies, and solid circles designate measurement of $^1B_u^+$ states energies. Lines are from quadratic fits ($E = A + B/N + C/N^2$) as explained in the text. Parameters of the fits are presented in Table S3, Supporting Information.

What about HCN Polymerization?

Dimerization of HCN in the gas phase: A theoretical mechanistic study

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ABSTRACT

Potential energy surfaces for the formation of covalently bound HCN dimers from two molecules of HCN or HNC were determined from CBS-QB3/APNO calculations. Several novel pathways, with and without the aid of protons, were found for the formation of iminoacetonitrile (HN=CHCN), an intermediate in adenine synthesis from HCN by oligomerization. Covalent C–C or C–N bonds between the two monomers were formed after rearrangement of bimolecular complex intermediates. Energetic and kinetic analyses suggest that the proton-catalyzed dimerizations substantially lower reaction barriers but cannot occur efficiently under interstellar conditions.

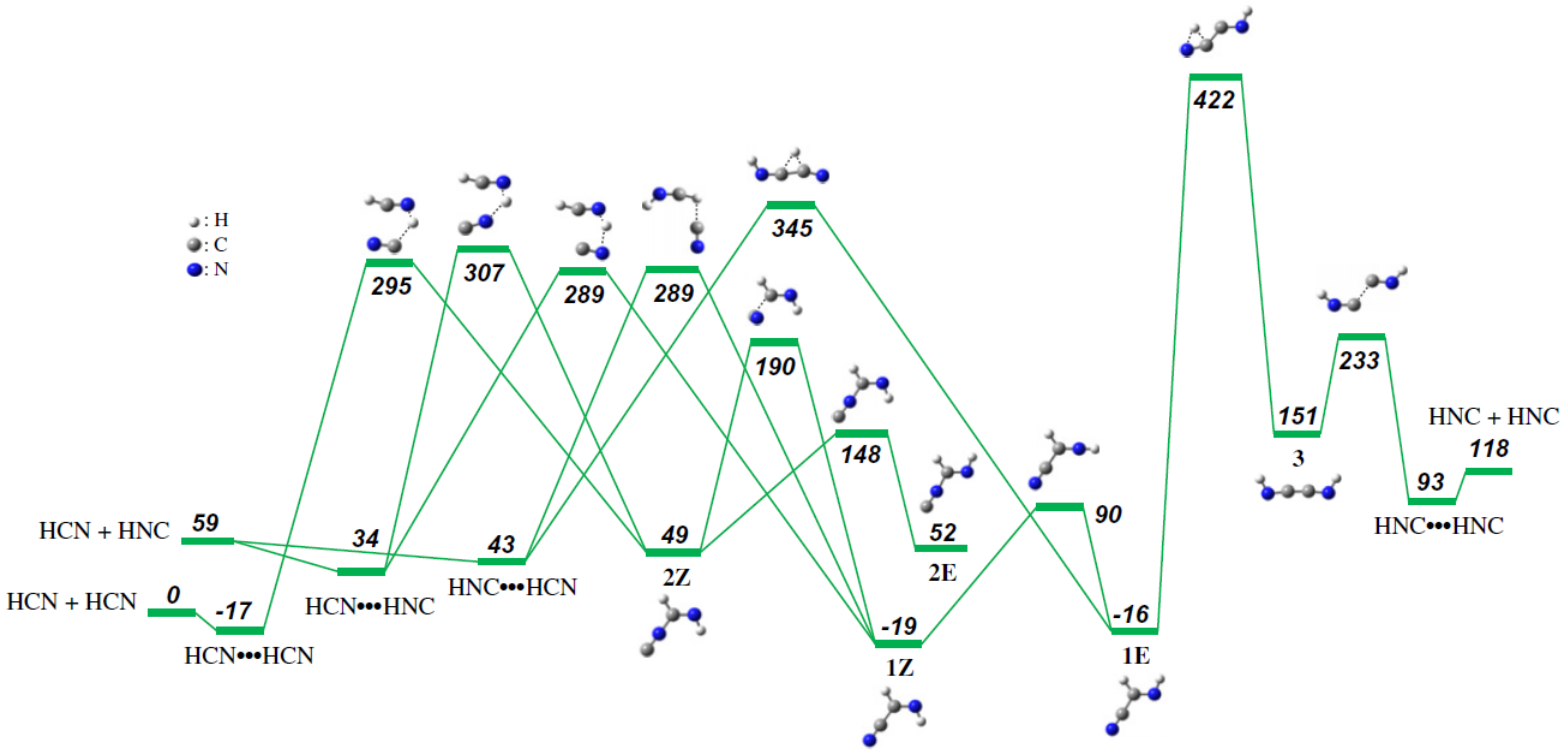

Figure 1. Potential energy diagram for the formation of covalently bound HCN dimers from two molecules of HCN or HNC, derived from CBS-QB3 calculations. The energies are in kJ mol^{-1}.

Acknowledgements:

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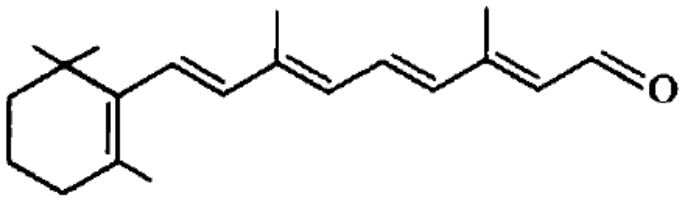
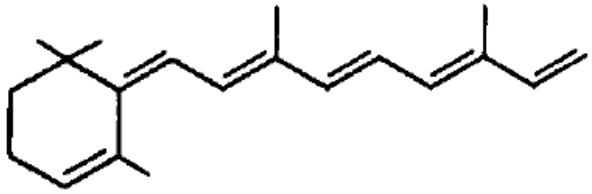
David Usher

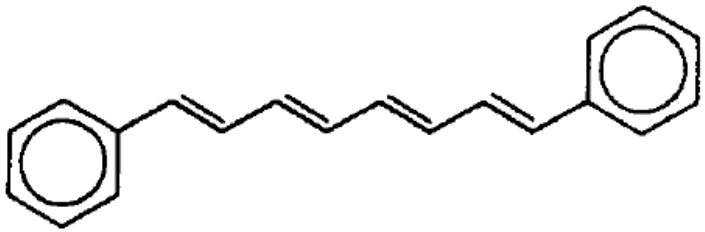
Polyene Photochemistry (Kohler)



All-*trans* retinal

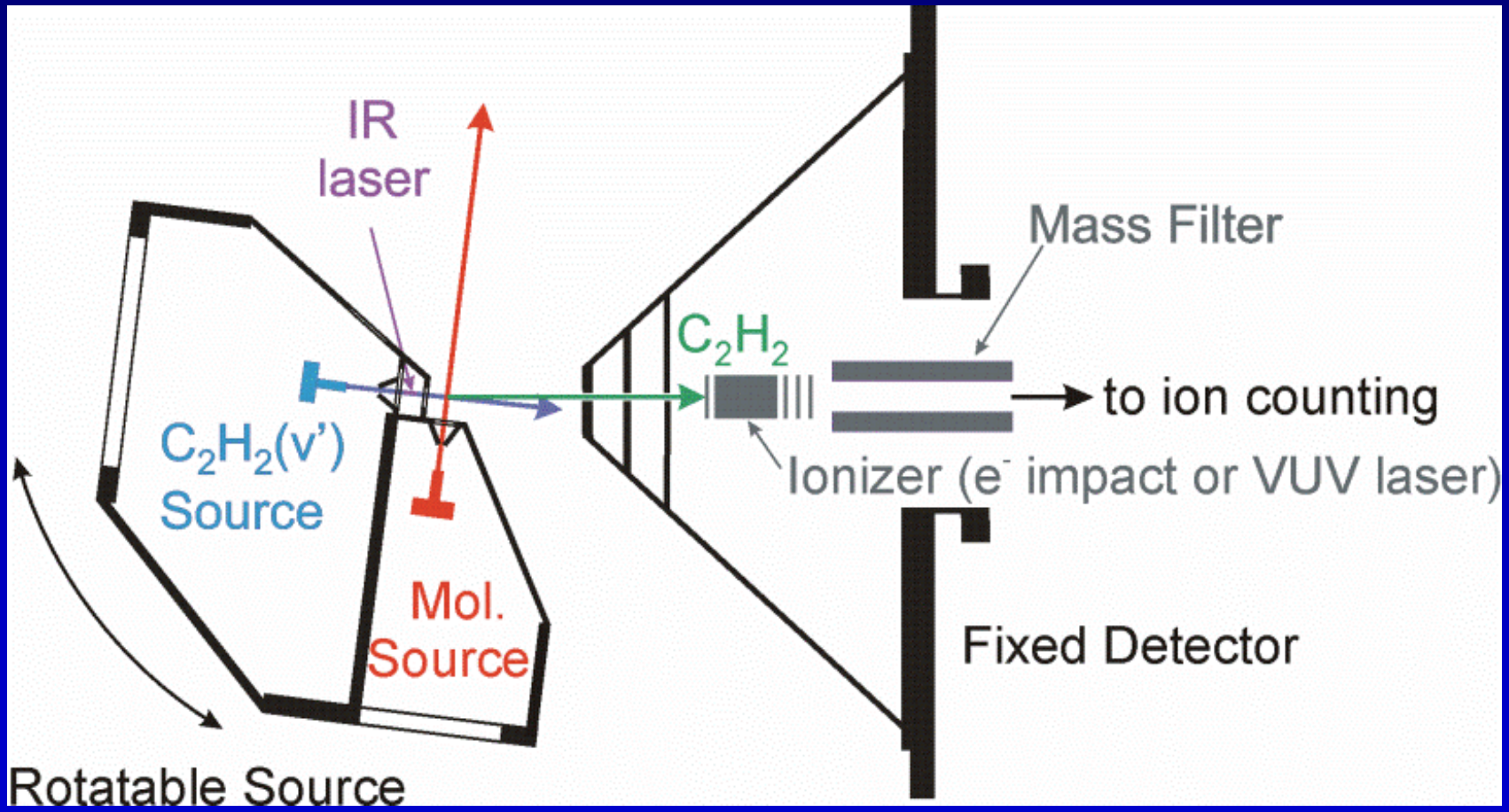


Anhydrovitamin A



Diphenyloctatetraene

Nonreactive Scattering of C_2H_2 (v) with other molecules



Polymerization of Acetylene?

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, E10005, doi:10.1029/2009JE003369, 2010

Detection and mapping of hydrocarbon deposits on Titan

Roger N. Clark,[1] John M. Curchin,[1] Jason W. Barnes,[2] Ralf Jaumann,[3] Larry Soderblom,[4] Dale P. Cruikshank,[5] Robert H. Brown,[6] Sébastien Rodriguez,[7] Jonathan Lunine,[8] Katrin Stephan,[3] Todd M. Hoefen,[1] Stéphane Le Mouélic,[9] Christophe Sotin,[10] Kevin H. Baines,[10] Bonnie J. Buratti,[10] and Philip D. Nicholson[11]

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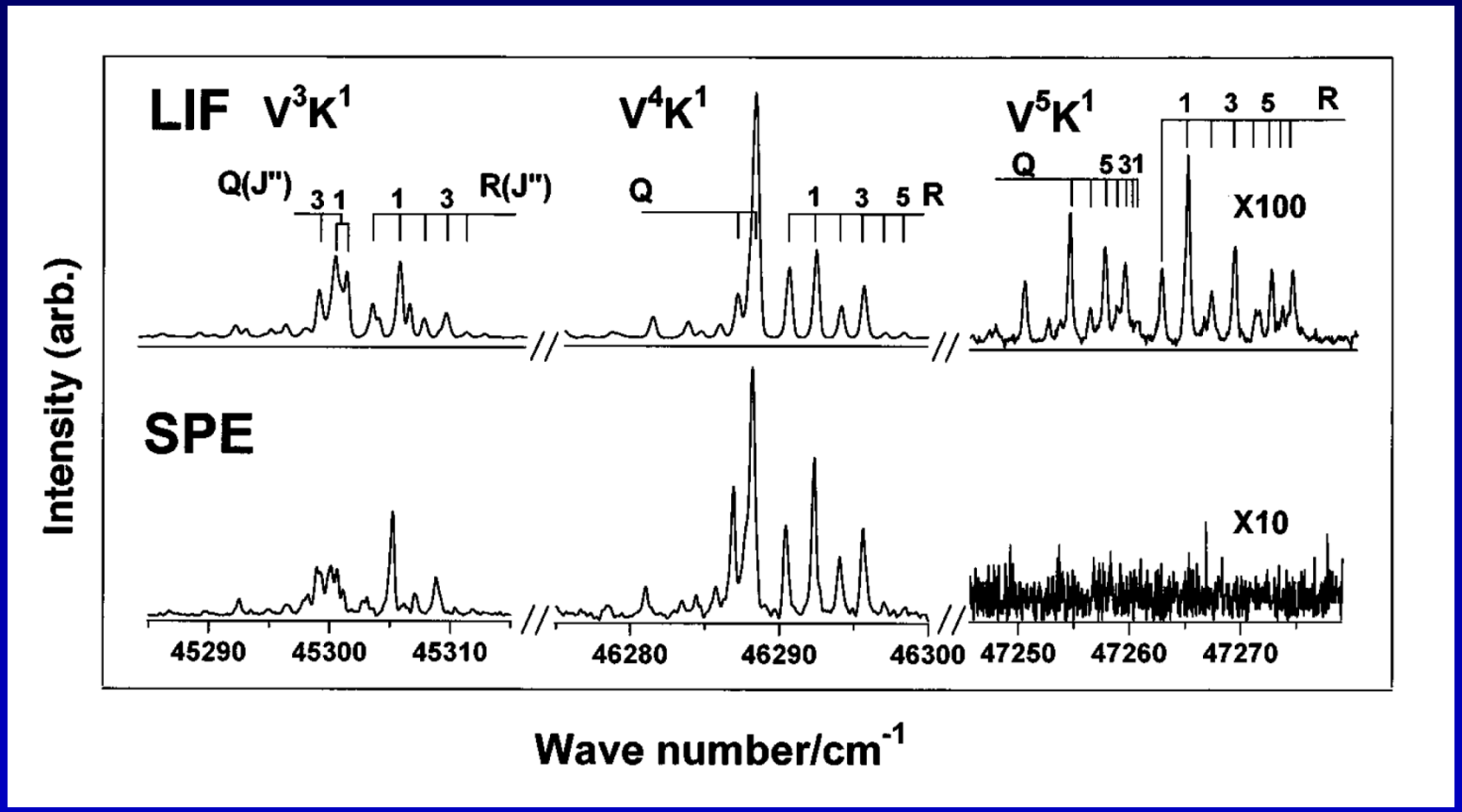
[1] We report the identification of compounds on Titan's surface by spatially resolved imaging spectroscopy methods through Titan's atmosphere, and set upper limits to other organic compounds. We present evidence for surface deposits of solid benzene (C_6H_6), solid and/or liquid ethane (C_2H_6), or methane (CH_4), and clouds of hydrogen cyanide (HCN) aerosols using diagnostic spectral features in data from the Cassini Visual and Infrared Mapping Spectrometer (VIMS). Cyanoacetylene (2-propynenitrile, IUPAC nomenclature, HC_3N) is indicated in spectra of some bright regions, but the spectral resolution of VIMS is insufficient to make a unique identification although it is a closer match to the feature previously attributed to CO_2. We identify benzene, an aromatic hydrocarbon, in larger abundances than expected by some models. Acetylene (C_2H_2), expected to be more abundant on Titan according to some models than benzene, is not detected. Solid acetonitrile (CH_3CN) or other nitriles might be candidates for

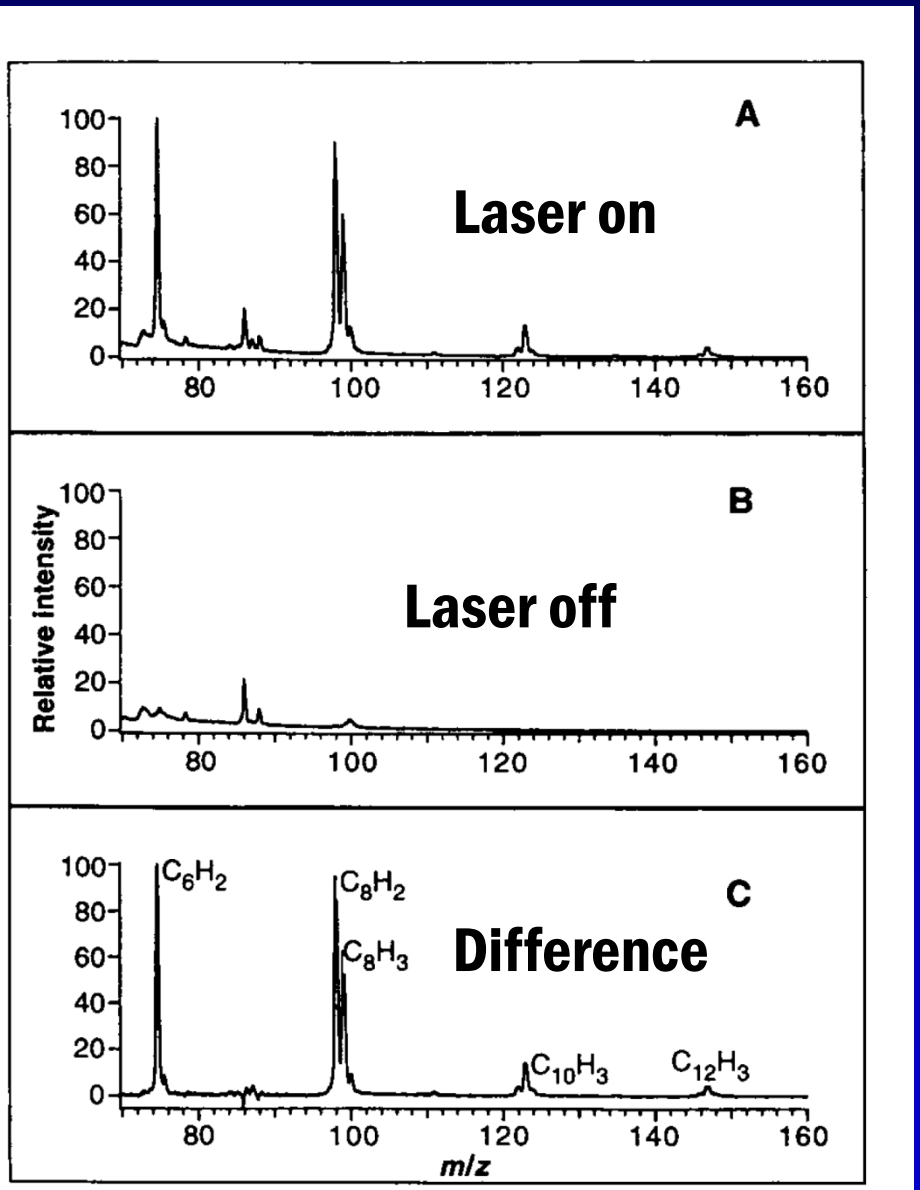
UV Excitation Produces Triplet Acetylene

J. Chem. Phys 106, 5292 (1997)



No triplets formed above 5.86 eV:
Due to onset of photodissociation

Zwier, Science 258, 1630 (1992)



SCIENCE • VOL. 258 • 4 DECEMBER 1992

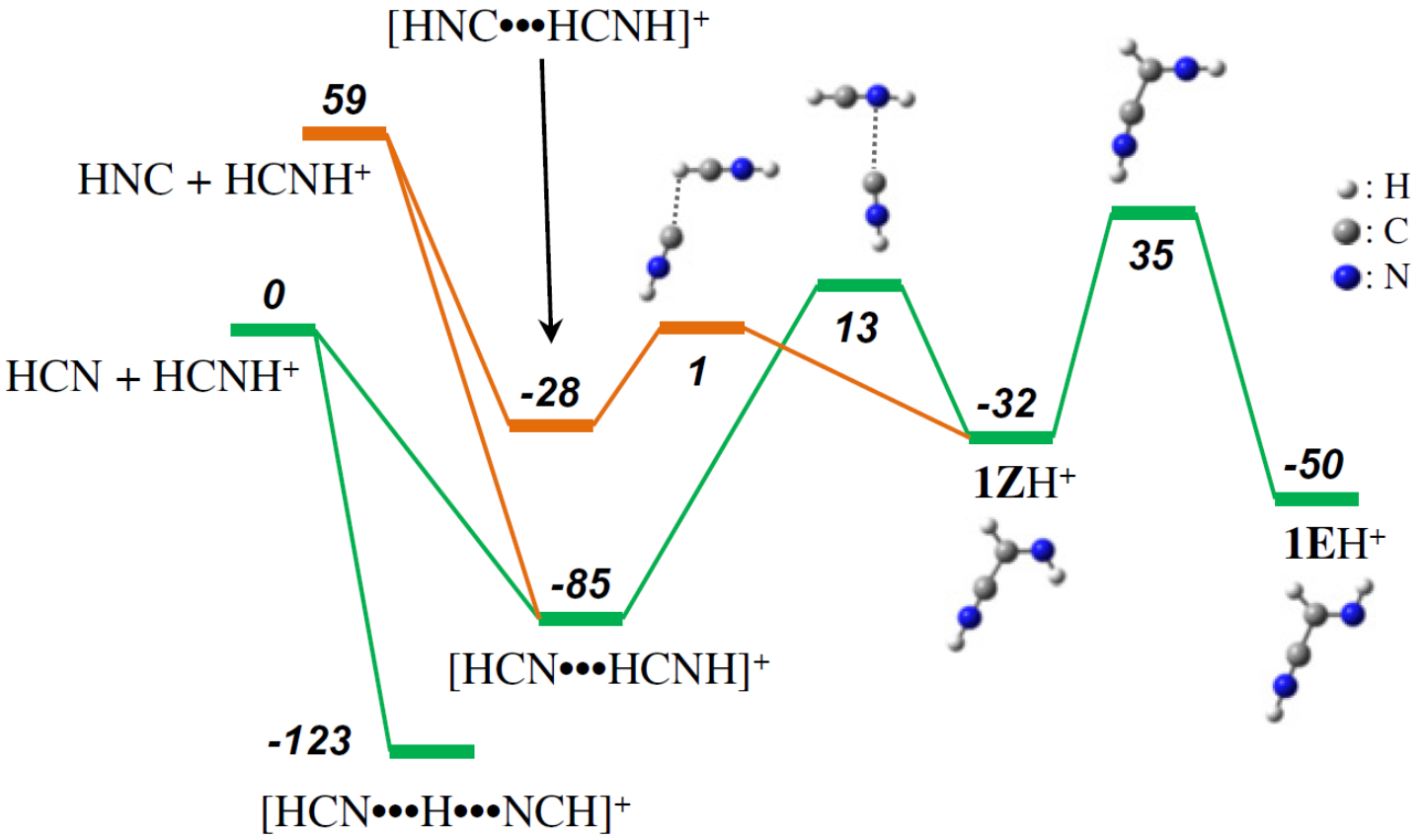


Figure 3. Potential energy diagram for the formation of **1Z**H^+ from HCN + $HCNH^+$ or HNC + $HCNH^+$, derived from CBS-QB3 calculations. The energies are in kJ mol^{-1}.