

OHIO STATE UNIVERSITY INTERNATIONAL 50th SYMPOSIUM ON MOLECULAR SPECTROSCOPY JUNE 12-16, 1995

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Special Sessions

Since this year marks the 50th consecutive annual meeting of the Ohio State University International Symposium on Molecular Spectroscopy, we have planned a number of events to commemorate the occasion. Highlighting these events will be a plenary session all day Wednesday, June 14. The session will feature opening and closing addresses by the Directors of the two agencies in the United States most directly responsible for sponsoring the research presented at the Symposium and the Symposium itself, respectively **Neal Lane** of the National Science Foundation and **Gerald Iafrate** of the Army Office of Research. The heart of the plenary session will feature lectures by eight Nobel Laureates: **Dudley Herschbach**, Harvard; **Gerhard Herzberg**, NRCC; **Yuan T. Lee**, Academia Sinica; **Charles H. Townes**, University of California at Berkeley; **John Polanyi**, University of Toronto; **George Porter**, Imperial College, London; **Norman F. Ramsey**, Harvard; **Kenneth G. Wilson**, The Ohio State University. Work of these Laureates has either been in molecular spectroscopy or strongly influenced by it. We expect this to be a truly memorable session.

The plenary session on Monday, June 12 will feature talks by **Ian Mills**, Reading University; **David Nesbitt**, JILA; and this year's Coblentz Award winner, **David Rakestraw**, Sandia. This session will also include presentation of the Rao Prizes described below.

This year will feature, as usual, sessions devoted to special topics. **John W. Johns**, NRCC, is organizing a symposium on fourier transform spectroscopy: techniques and instrumentation. It will feature talks by **Kelly Chance**, Smithsonian Astrophysical Observatory; **D. Chris Benner**, College of William and Mary; and **Daniel Grischkowsky**, Oklahoma State University. A symposium on Photoionization Spectroscopy (REMPI, ZEKE, etc.) is being organized by **Edward Grant**, Purdue and will feature invited talks by himself and **John Hepburn**, Waterloo. A symposium on Theory is being organized by **Russell Pitzer**, The Ohio State University and will feature an invited talk by **Timothy J. Lee**, NASA Ames Research Center. The year of 1995 is also the 50th Anniversary of the founding of the Microwave Laboratory by Walter Gordy at Duke. A special session organized by **Frank C. DeLucia**, The Ohio State University, will be held in honor of this occasion.

TJ03 15 min 2:04

NEGATIVE ANHARMONICITIES OF THE BENDING VIBRATION OF CCH AND THE TRANS-BENDING VIBRATION OF THE ACETYLENE CATION, JIM JR-MIN LIN AND YEN-CHU HSU

The levels of the bending vibration ($\nu_2=1-11$) of $\text{CCH}(\tilde{X}^2\Sigma^+)$ were determined by UV laser-induced fluorescence of the products of photolysis of acetylene at 193 nm. Large negative anharmonicity was found in the lowest five levels of the bending vibration. As the number of bending quanta increases, the anharmonicity decreases considerably. Levels $\nu_4=0-5$ of the trans-bending motion of the acetylene cation ($\tilde{X}^2\Pi_u$), isoelectronic with CCH, and its deuterated isotopomer have been determined by 1+1 PFI-ZEKE spectroscopy via a single rovibronic level of \tilde{A}^1A_u as an intermediate. Spectral analysis shows that negative anharmonicity was also present in the latter case.

Large negative anharmonicity of CCH is attributed to vibronic interaction¹ between $\tilde{X}^2\Pi$ and $\tilde{X}^2\Sigma^+$ as well as vibration-rotational interaction among the vibrational levels of the \tilde{X} state.² The potential-energy curve of the bending vibration of $\text{CCH}(\tilde{X})$ and that of the trans-bending vibration of C_2H_2^+ calculated by an ab initio method will be presented to show that negative anharmonicities of these molecules may be due to the flatness of the (zero-order) potential-energy curves. The Renner-Teller effect of the trans-bending vibration of the acetylene cation will be discussed.

1. E. Hirota, *Chem. Rev.* **92**, 141(1992).

2. Y.-C. Hsu, J. J.-M. Lin, D. Papoušek, and J.-J. Tsai, *J. Chem. Phys.* **98**, 6690(1993).

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TJ04 10 min 2:21

CHEMICAL KINETICS OF THE REACTION OF METHOXY WITH MOLECULAR OXYGEN FOR VARIOUS TEMPERATURES, PRESSURES AND BUFFER GASES,* P. MISRA, A.H. NUR, AND X. ZHU

The methoxy radical is produced in the troposphere as a chemical intermediate in the breakdown of methane by the hydroxyl radical. It reacts with molecular oxygen to form formaldehyde as a stable product. Various buffer gases, namely helium, argon and nitrogen, were used as carriers to transport the methyl nitrite precursor to the photolysis zone. Following excimer laser-induced photodissociation of the precursor, the methoxy radical was excited with a frequency-doubled Nd:YAG-pumped dye laser. Laser-induced fluorescence (LIF) signals were closely monitored under different conditions of temperature (22-150 °C) and oxygen pressures (0-40 torr). Temporal histories of the methoxy fluorescence decay were obtained by recording the LIF signal intensity as a function of increasing time delay between the photolysis and probe laser pulses. Stern-Volmer plots of the inverse first-order decay constant (τ^{-1}) versus oxygen pressure at different temperatures allowed determination of the rate constants for the reaction of methoxy with oxygen and the derivation of an appropriate Arrhenius expression over the temperature range 22-150 °C. Helium as buffer gas was able to quench the fluorescence from the methoxy radical more rapidly than either nitrogen or argon.

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