

Vibronic Spectroscopy of Cyclopentenone Isomers in Their Lowest Triplet Excited States



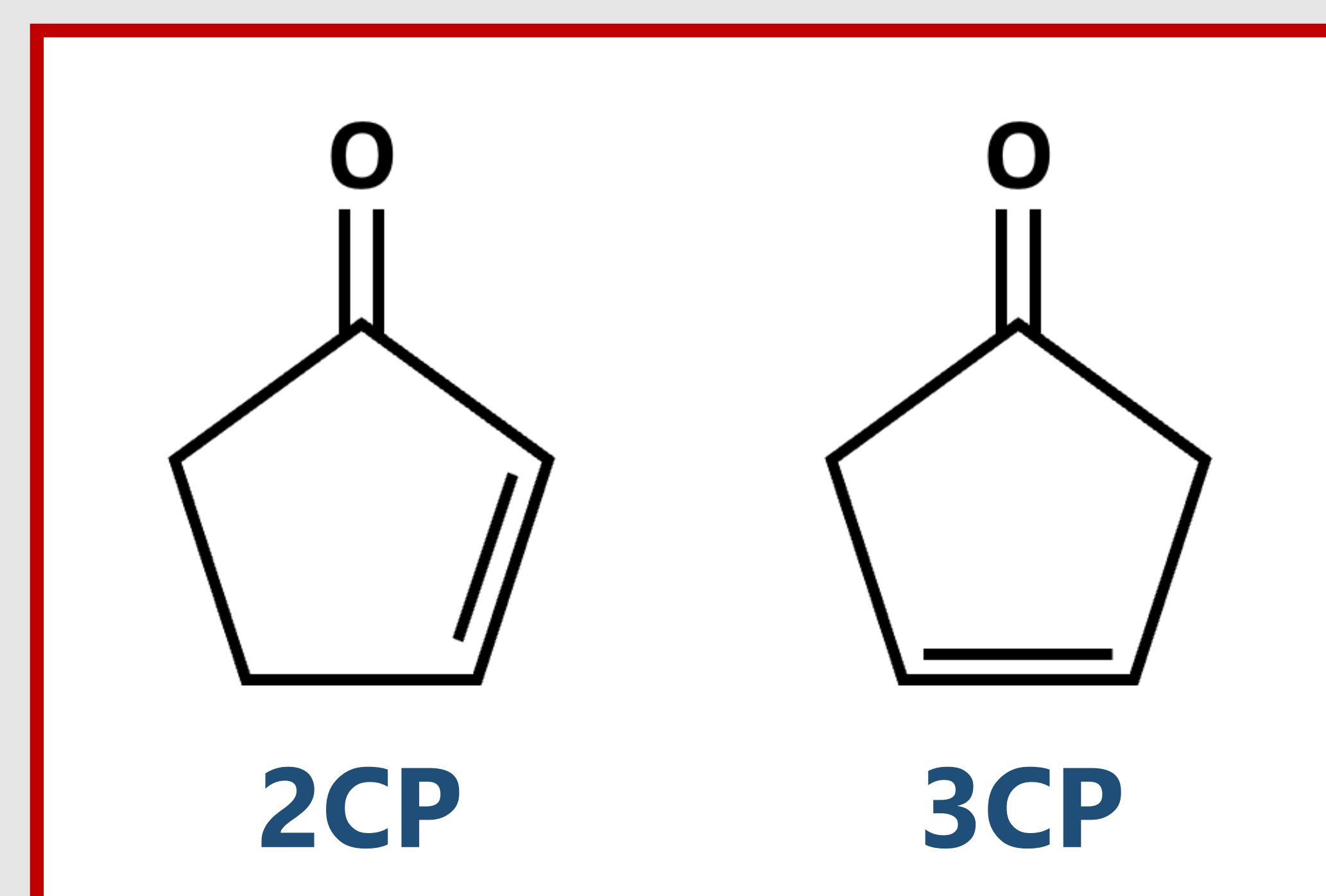
Alexander Narkiewicz-Jodko, Isaac Swenson, Jenna Trzebiatowski, Stephen Drucker

Department of Chemistry and Biochemistry
University of Wisconsin-Eau Claire, Eau Claire, Wisconsin 54701

Introduction

Molecular triplet states mediate a range of processes, including photochemistry, nonradiative decay, and combustion. Many of these triplet species are low-lying excited states, accessible via excitation in the near-UV region of the spectrum. In recent years, a large sector within the quantum-chemistry community has focused on efficient calculation of these states. High-resolution spectroscopy of triplet species provides critical benchmark information to test the accuracy of computed predictions. In turn, benchmarked computational methods offer valuable guidance for conducting spectral searches.

In this project, we used two highly sensitive techniques, Resonance Enhanced Multiphoton Ionization (REMPI) and Cavity Ringdown (CRD) Spectroscopy, to measure forbidden singlet-triplet vibronic band systems in cyclopentenone isomers. We studied 2-cyclopenten-1-one (2CP) and 3-cyclopenten-1-one (3CP). The functional groups of these monocycles offer a stringent test of modern computational methods, through comparison of measured vs. calculated triplet-state vibrational frequencies.



Computational Methods

We carried out harmonic-frequency calculations of the $T_1(n,\pi^*)$ state of 2CP using the TD-PBE0/def2-TZVPD and EOM-EE-CCSD/cc-pVTZ methods. For the latter, we estimated anharmonic corrections via a VPT2 calculation using TD-B3LYP/def2-TZVP.

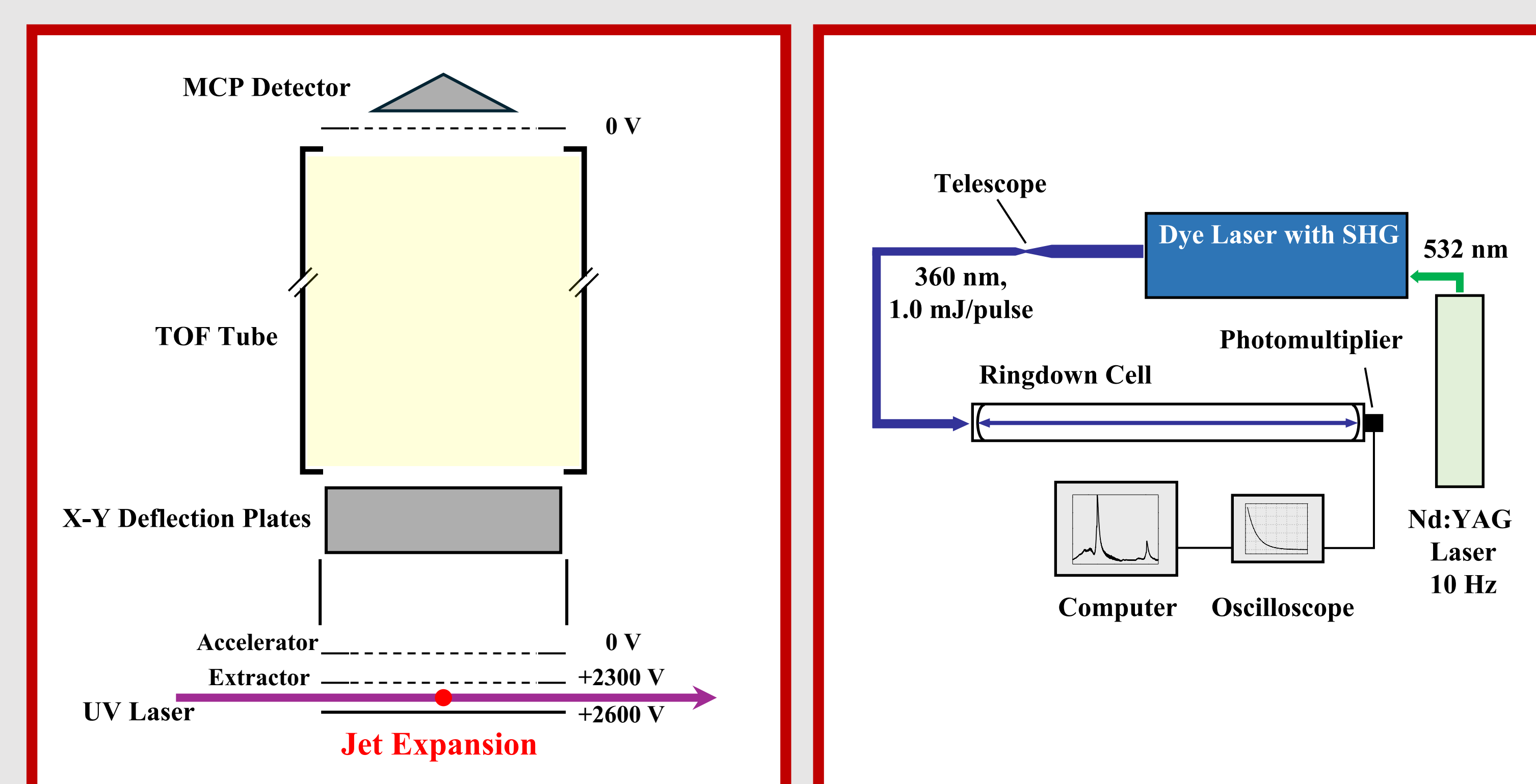
To guide our CRD spectral searches of 3CP, we calculated the 0-0 excitation energy of the $T_1(n,\pi^*) \leftarrow S_0$ transition. We first calculated the adiabatic excitation energy, by conducting geometry optimizations of the T_1 and S_0 states using (EOM-EE-)CCSD/def2-TZVPP methods within the frozen-core approximation. We calculated single-point energies of the optimized T_1 and S_0 structures using UHF CCSD(T)/aug-pwCVTZ (without the frozen-core approximation). To obtain the 0-0 excitation energy, we added (TD)-PBE0/cc-pVTZ zero-point vibrational energy corrections to the adiabatic values.

We used the Q-Chem¹ computational chemistry package for the geometry optimizations and DFT-based frequency calculations. We used CFOUR² for CCSD-based frequency calculations and CCSD(T) single-point energies.

Experiment

To record the REMPI spectrum of 2CP, we used a pulsed dye laser in a 1+2 single-wavelength excitation scheme. The photoions are accelerated into a zero-field time-of-flight tube and are monitored at the parent mass using an MCP detector. The molecular source is a supersonic free-jet expansion with an effective vibrational temperature of about 20 K.

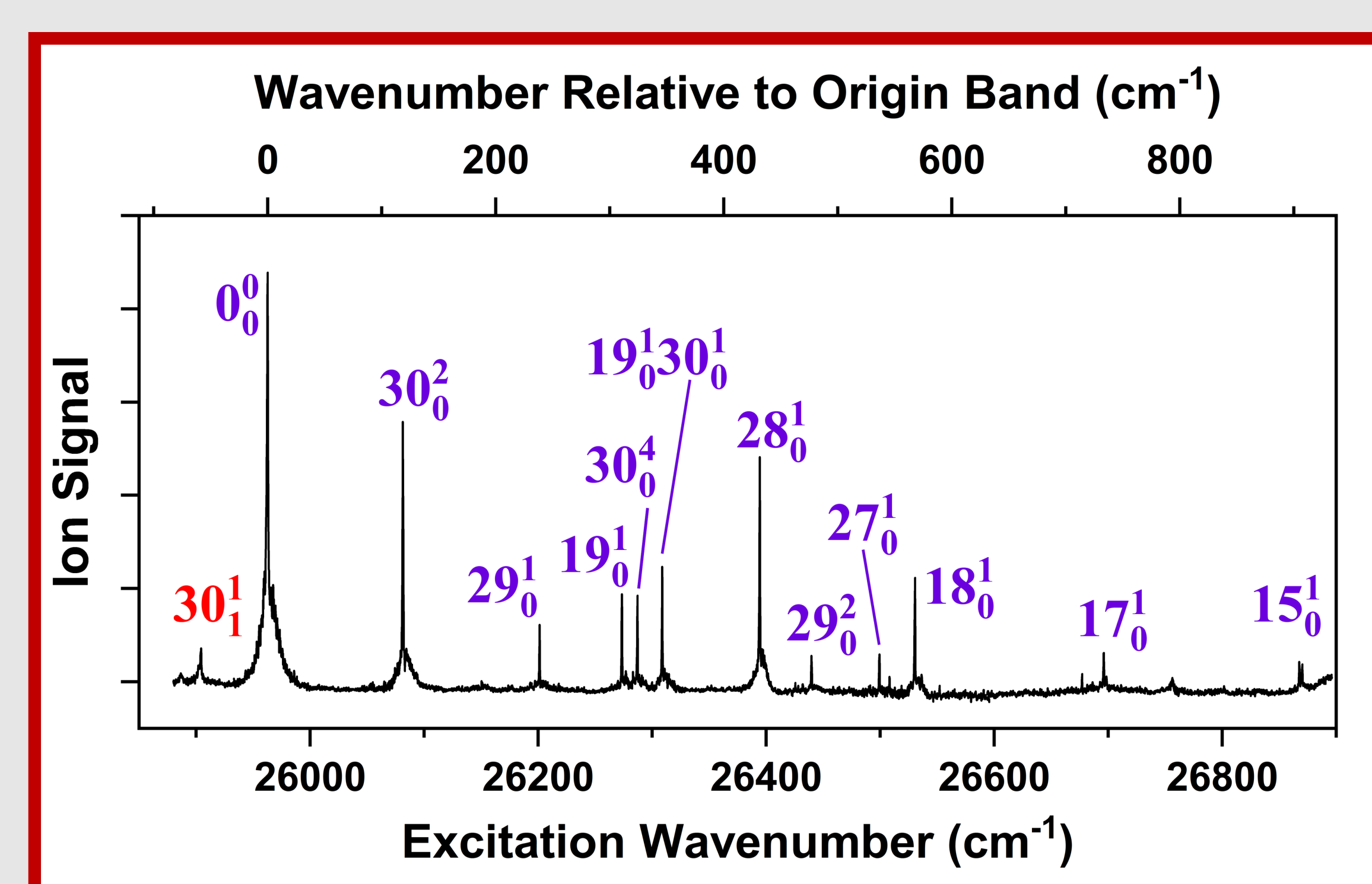
For CRD studies of 3CP, a dye laser equipped with a second-harmonic generator produces laser pulses around 360 nm. The light is collimated with a Keplerian telescope and enters a 1-m sample cell constructed of Delrin. The room-temperature cell is bounded by high-reflectivity mirrors ($R=0.9995$). A photomultiplier detects ringdown pulses exiting the cell. An oscilloscope PC expansion card monitors the ringdown signal and sends it to a fitting routine to determine the exponential rate constant.



REMPI Spectrum of 2CP

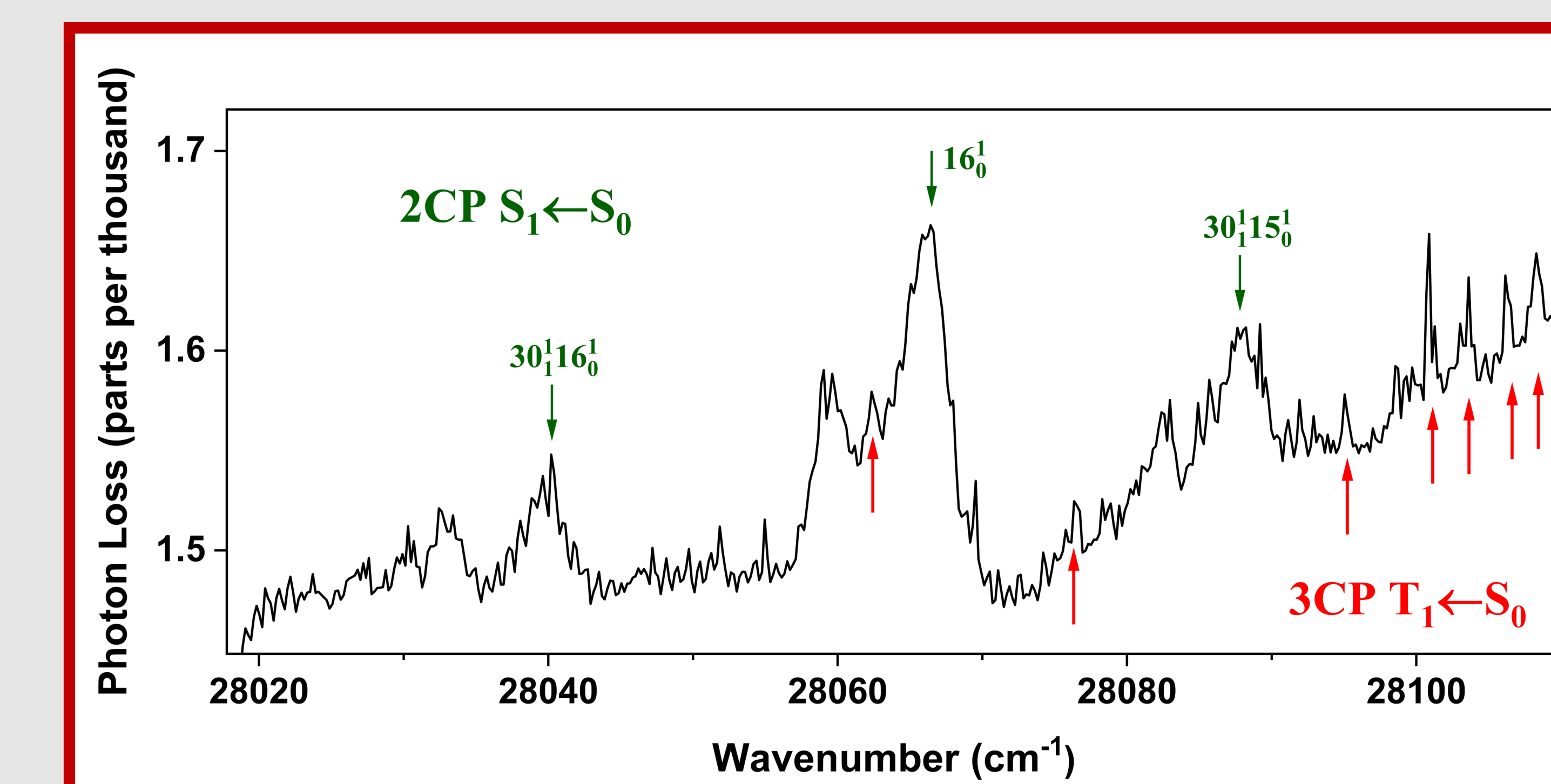
The REMPI spectrum of the 2CP $T_1(n,\pi^*) \leftarrow S_0$ band system is shown below. This spectrum complements our previous measurement³ using jet-cooled phosphorescence excitation spectroscopy. Vibronic information in the earlier study was limited because of diminished emission quantum yield at higher $T_1(n,\pi^*)$ excitation energies. The 3-photon REMPI method eliminates this problem because ionization occurs within the same laser pulse as $T_1(n,\pi^*)$ excitation.

Vibronic assignments in the REMPI spectrum yielded fundamental frequencies for seven vibrational modes in the T_1 state, including ring twisting (ν_{29}), carbonyl wagging (ν_{19} and ν_{28}), along with several in-plane ring modes.



CRD Spectrum of 3CP

The room-temperature CRD spectrum of 3CP vapor (6 torr) near 356 nm is shown below. The vapor contains about 2% 2CP, due to impurity of the liquid sample in equilibrium with the vapor. The peaks marked below in green are previously assigned⁴ vibronic transitions within the relatively strong (spin allowed) $S_1(n,\pi^*) \leftarrow S_0$ band system. The much sharper features marked in red are assigned to the $T_1(n,\pi^*) \leftarrow S_0$ transition of 3CP. Work is in progress to assign the origin band of this transition. Based on the absence of sharp features in longer-wavelength regions, the origin band is assumed to be between 27700 and 28100 cm^{-1} .



Key Computational Findings

Vibrational Frequencies of T_1 2CP: we used the seven $T_1(n,\pi^*)$ frequencies obtained from the REMPI spectrum of 2CP to test predictions of the EOM-EE-CCSD *ab initio* as well as the TD-PBE0 density functional method. We used VPT2 to provide an anharmonic correction to the EOM-EE-CCSD results and an optimized scale factor⁵ (0.965) to correct the PBE0 results. The mean absolute deviation between measured and predicted fundamental frequencies is 19.9 cm^{-1} for the EOM calculation and 9.5 cm^{-1} for the PBE0 calculation. The superior performance of PBE0 is notable, given its significantly *lower* computational cost.

0-0 Excitation Energy of T_1 3CP: to estimate the origin-band position for the $T_1(n,\pi^*) \leftarrow S_0$ transition of 3CP, we used the approach of Loos and Jacquemin,⁶ substituting CCSD(T) methods for the very expensive CC3 "gold standard." The resulting 0-0 band prediction is 27710 cm^{-1} , which agrees remarkably well with the range (27700 to 28100 cm^{-1}) ascertained from the CRD spectrum.

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References. (1) Y. Shao *et al.*, *Q-Chem 5.2*, Q-Chem, Inc., Pleasanton, Calif. (2019). (2) *CFOUR v. 2.1*, a quantum-chemical program package, written by J. F. Stanton *et al.* (3) N. R. Pillsbury, T. S. Zwier, R. H. Judge, and S. Drucker, *J. Phys. Chem. A* **2007**, *111*, 8357. (4) R. D. Gordon and D. R. Orr, *J. Mol. Spec.* **1988**, *129*, 24. (5) J. Liu and W. Liang, *J. Chem. Phys.* **2011**, *135*, 184111. (6) P. Loos and D. Jacquemin, *J. Chem. Theory Comput.* **2019**, *15*, 2481.