Lowest triplet ($\pi, \pi^*$) electronic state of acrolein: Determination of structural parameters by cavity ringdown spectroscopy and quantum-chemical methods

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The cavity ringdown absorption spectrum of acrolein (propanal, $\text{CH}_2=\text{CH}—\text{CH}=\text{O}$) was recorded near 412 nm, under bulk-gas conditions at room temperature and in a free-jet expansion. The measured spectral region includes the $0\nu^0_0$ band of the $T_1(n, \pi^*) \leftarrow S_0$ system. We analyzed the $0\nu^0_0$ rotational contour by using the STROTA computer program [R. H. Judge et al., J. Chem. Phys. 103, 5343 (1995)], which incorporates an asymmetric rotor Hamiltonian for simulating and fitting singlet-triplet spectra. We used the program to fit $T_1(n, \pi^*)$ inertial constants to the room-temperature contour. The determined values $(\text{cm}^{-1})$, with $2\sigma$ confidence intervals, are: $A = 1.662 \pm 0.003$, $B = 0.1485 \pm 0.0006$, $C = 0.1363 \pm 0.0004$. Linewidth analysis of the jet-cooled spectrum yielded a value of $14 \pm 2$ ps for the lifetime of isolated acrolein molecules in the $T_1(n, \pi^*)$, $v = 0$ state. We discuss the observed lifetime in the context of previous computational work on acrolein photochemistry. The spectroscopically derived inertial constants for the $T_1(n, \pi^*)$ state were used to benchmark a variety of computational methods. One focus was on complete active space methods, such as complete active space self-consistent field (CASSCF) and second-order perturbation theory with a CASSCF reference function (CASPT2), which are applicable to excited states. We also examined the equation-of-motion coupled-cluster and time-dependent density function theory excited-state methods, and finally unrestricted ground-state techniques, including unrestricted density functional theory and unrestricted coupled-cluster theory with single and double and perturbative triple excitations. For each of the above methods, we or others [O. S. Bokareva et al., Int. J. Quantum Chem. 108, 2719 (2008)] used a triple zeta-quality basis set to optimize the $T_1(n, \pi^*)$ geometry of acrolein. We find that the multiconfigurational methods provide the best agreement with fitted inertial constants, while the economical unrestricted Perdew-Burke-Ernzerhof exchange-correlation hybrid functional (UPBE0) technique performs nearly as well. © 2013 American Institute of Physics.

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I. INTRODUCTION

Conjugated enone molecules participate in a variety of photochemical processes, typically mediated by low-energy triplet excited states of $^3(n, \pi^*)$ or $^3(\pi, \pi^*)$ configuration. The triplet species play a significant role in enone photochemistry, in part because they are readily accessible via inter-system crossing from a singlet photoexcited state. Also, in a solution-phase environment, those enone molecules possessing skeletal rigidity are known to be metastable with respect to radiative or nonradiative decay to the ground state, and therefore these species are susceptible to collisional encounters with other molecules.

Acrolein, $\text{CH}_2=\text{CH}—\text{CH}=\text{O}$, is the smallest of the enone molecules and serves as a starting point for investigating their excited-state dynamics. Acrolein and its substituted derivatives have been the subject of numerous experimental and computational investigations aimed at understanding the roles of various excited states in the photochemistry of enones. Reguero et al. conducted an extensive complete active space self-consistent field (CASSCF) computational investigation of the photophysical fate of $s$-trans acrolein following excitation to the $S_1(n, \pi^*)$ state. Reguero’s computations predict that when the $S_1$ state is prepared by photoexcitation in a solution-phase environment, it decays via a series of surface crossings and conical intersections to the $T_1(n, \pi^*)$ state. As seen in Fig. 1, this is a diradical species in which the $\text{CH}_2$ group is twisted 90° with respect to original molecular plane. The $\pi^*$ antibonding orbital is nominally localized at the $\text{C}=$=$\text{C}$ moiety, and occupancy of the $\pi^*$ antibonding orbital allows the $\text{CH}_2$ group to twist, thereby minimizing repulsion between the two unpaired electrons of the diradical.

In solution, this fully “relaxed” $T_1(n, \pi^*)$ species has a very short lifetime for a triplet state, assumed to be on the order of 10 ns, based on transient absorption experiments of substituted acrolein derivatives such as methyl vinyl ketone. The short lifetime of the twisted $T_1(n, \pi^*)$ state in acrolein is attributed to rapid intersystem crossing that populates highly vibrationally excited levels of the $S_0$ ground state. In acrolein derivatives with nonequivalent substitutions at the $\text{CH}_2$ group, this nonradiative decay from

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the twisted $T_1(\pi, \pi^*)$ state to the planar $S_0$ state can result in cis–trans isomerization.\textsuperscript{7} Structurally rigid acrolein derivatives, such as cyclic enones, have slower rates of intersystem crossing and can therefore undergo bimolecular photochemistry.

In acrolein, the calculated\textsuperscript{7} sequence of surface crossings leading from the planar $S_1(n, \pi^*)$ state to the twisted $T_1(\pi, \pi^*)$ state is intricate but centrally involves the lowest-lying triplet $3(n, \pi^*)$ state. The present paper is focused on our spectroscopic investigation of the $3(n, \pi^*)$ state. The calculations of Reguero\textsuperscript{7} and others\textsuperscript{8–13} indicate that in both the $1(n, \pi^*)$ and $3(n, \pi^*)$ states, the chromophore is localized on the C=O rather than the C=C moiety, and so the molecule remains planar for both singlet and triplet $\pi^* \rightarrow n$ excitation. We will refer to the $3(n, \pi^*)$ state as $T_1(n, \pi^*)$, with the $T_1$ designation indicating that it is the lowest-lying triplet state that has a planar equilibrium geometry, as shown in Fig. 1. If the CH$_2$ group of this $3(n, \pi^*)$ species is twisted out of planarity, it becomes higher in energy than the $3(\pi, \pi^*)$ state in most regions of the coordinate space.\textsuperscript{7,11,12} We refer to the latter configuration as $T_1$ when the triplet species is in its relaxed, twisted geometry.

The numerous calculated regions on the $S_1$ and $T_1$ potential surfaces allowed Reguero \textit{et al.}, in 1994, to map out photochemical pathways available to acrolein.\textsuperscript{7} Since then, increasingly efficient computational methods for treating excited states have been developed, and in recent years\textsuperscript{10–13} a variety of these techniques have been applied to acrolein. Tests of these recent calculations have relied primarily on spectroscopic information available for the $S_1(n, \pi^*)$ singlet state.\textsuperscript{14–16} However, the triplet states of acrolein and other enones have a more direct bearing on their photochemistry. It is highly desirable to characterize the triplet states spectroscopically, as a check on the computational approaches that hold the most promise for describing the mechanistic details of enone photochemistry.

In general, spectroscopic investigations of molecular triplet states have been sparse, essentially because singlet-triplet transitions originating in the ground state are nominally spin-forbidden. Moreover for acrolein, high-sensitivity techniques based on light emission, such as phosphorescence excitation, are implausible because of the fast nonradiative processes discussed above. Previous investigations of triplet acrolein have employed absorption spectroscopy using long pathlengths (10 m) and relatively high vapor pressures (100–150 Torr) of heated samples. In 1971 Bair, Goetz, and Ramsay assigned eight vibronic bands between 404 nm and 422 nm to the $T_1(n, \pi^*) \rightarrow S_0$ system of $s$-trans acrolein.\textsuperscript{17}

This work included medium-resolution (0.008 nm or 0.5 cm$^{-1}$) absorption and magnetic rotation scans of the $0_0^0$ band at 412.2 nm that confirmed the singlet-triplet nature of the transition. In a subsequent study, Osborne and Ramsay confirmed the vibronic assignments of Bair \textit{et al.} by recording the absorption spectra of acrolein along with its $–d_1$ (CH$_2$=CH–CD=O) isotopomer.\textsuperscript{15}

After the era of Ramsay’s work on acrolein, the cavity ringdown (CRD) technique was invented and has since become an attractive option for absorption spectroscopy.\textsuperscript{16–20} Though CRD is not a dark-background technique, its near-immunity to laser intensity fluctuations leads to very low noise levels. In 2004, we used CRD spectroscopy to record several bands of the $T_1(n, \pi^*) \leftarrow S_0$ system of $s$-trans acrolein.\textsuperscript{20} The spectrum was recorded at room temperature using an acrolein pressure of 10 Torr in a 1-m cell. The pulsed dye laser used for the experiment afforded a spectral resolution of 0.1 cm$^{-1}$. In a previous paper,\textsuperscript{20} we used this spectrum to discuss the advantages of CRD over conventional methods of absorption spectroscopy.

A portion of the 2004 CRD spectrum, showing the $0_0^0$ band of the $T_1(n, \pi^*) \leftarrow S_0$ transition, is shown in Fig. 2. The high signal-to-noise ratio (S/N, about 1500), along with the medium-high resolution of the dye laser, afford a good deal of structure, which is amenable to rotational contour analysis. Rovibronic selection rules for singlet-triplet transitions are complicated because the oscillator strength derives from spin-orbit interactions with nearby singlet states.\textsuperscript{21} However, Judge \textit{et al.} have written a reliable program, STROTA, for simulating or fitting the rotational contours of such

![FIG. 1. Schematic illustration of potential-energy curves for twisting of the CH$_2$ group in the lowest triplet excited states of acrolein. The energy scale is based on calculations of Reguero \textit{et al.}.\textsuperscript{7}](image)

![FIG. 2. Cavity ringdown absorption spectrum of the $0_0^0$ band of the $T_1(n, \pi^*) \leftarrow S_0$ transition of acrolein. The spectrum was recorded using a 1-m cell at room temperature. The pressure of the gaseous acrolein sample was 10 Torr.](image)
transitions.\textsuperscript{22} Judge recently modified\textsuperscript{23} the original program, suitable for molecules of orthorhombic symmetry, so that it applies to molecules with \textit{C}_2 symmetry, such as acrolein.

We have used the \textsc{strotia} program to conduct a rotational contour analysis of the 0\textsubscript{0} band observed in the room-temperature $T_1 \leftarrow S_0$ CRD spectrum. This analysis offers, for the first time, an experimental test of $T_1(n, \pi\ast)$ equilibrium geometries determined from \textit{ab initio} and DFT calculations. We compare here the fitted $T_1$ inertial constants with those deriving from an assortment of computational methods.

Of the computational methods we test here, the multireference CASPT2 method represents the highest level of theory. Godunov\textsuperscript{11} previously used CASPT2 to optimize the $T_1(n, \pi\ast)$ geometry of acrolein. Page and Olivucci,\textsuperscript{9} Godunov,\textsuperscript{11} and Guido\textsuperscript{13} also used less expensive methods applicable to excited states, such as CASSCF and time-dependent density function theory (TD-DFT) (the latter with various functionals), to calculate the optimized geometry of the $S_1(n, \pi\ast)$ state, but they did not report the geometry of the $T_1(n, \pi\ast)$ state using these methods. As part of the present study, we used CASSCF and TD-DFT, as well as equation-of-motion coupled-cluster (EOM-EE-CCSD), to perform geometry optimizations for the $T_1(n, \pi\ast)$ state.

Godunov\textsuperscript{11} also conducted this calculation using the high-level unrestricted CCSD(T) ground-state method (UCCSD(T)), which is applicable to the \textit{3}(n, \pi\ast) state of acrolein because, in the planar geometry, it is the lowest-energy configuration of its spin multiplicity. To complement Godunov’s UCCSD(T) calculation, we have used the more economical unrestricted DFT (UDFT) methods to optimize the geometry of the $T_1(n, \pi\ast)$ state.

A final component of this work addresses the complicated branch structure of the $T_1 \leftarrow S_0$ 0\textsubscript{0} band contour. The rotational selection rules for this transition are only loosely constraining,\textsuperscript{21} leading to spectral congestion in the room-temperature CRD spectrum. The situation is worsened by the presence of vibronic hot bands overlapping the 0\textsubscript{0} origin band. To reduce the spectral congestion, we recorded the acrolein CRD spectrum under the cooling conditions of a supersonic free-jet expansion.

The low-temperature simulations provide a check on the fitting procedure we employed to obtain excited-state inertial constants from the room-temperature rotational contour. The jet-cooled contour also provides the first experimental estimate of the lifetime of the $T_1$ state ($\nu = 0$ level) of acrolein under isolated-molecule conditions. This result complements the findings of Paulisse \textit{et al.},\textsuperscript{16} who recorded the $S_1(n, \pi\ast) \leftarrow S_0$ CRD spectrum of acrolein under similar jet-cooled conditions. Their investigation produced an estimate of the $S_1(n, \pi\ast)$ lifetime. We will discuss the experimentally determined lifetimes of the $T_1(n, \pi\ast)$ and $S_1(n, \pi\ast)$ states in the context of previous computational work on the photophysical and photochemical pathways available to acrolein.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Experimental

The apparatus for recording room-temperature CRD spectra has been described in detail previously.\textsuperscript{20} Briefly, a 6-

ns pulse from a 10-Hz Nd:YAG-pumped (Continuum Surelite II) tunable dye laser (Lambda-Physik ScanMate 2E) is sent into a 1-m optical cavity containing a gaseous sample and bounded by high-reflectivity ($R \geq 0.997$) concave mirrors (VLOC) with 6-m radii of curvature. The light entering the cavity has a pulse energy of approximately 2 mJ near 410 nm. A photodiode measures the ringdown decay of the light as it exits the optical cavity. The detector signal is sent to a digital oscilloscope, uploaded to a computer, and analyzed to determine the best-fitting exponential decay constant, along with amplitude and vertical offset.

To record the room-temperature spectrum reported here, the acrolein sample (Aldrich) was purified by simple distillation under nitrogen. The distillate was then subjected to several freeze-pump-thaw cycles. After the final freezing step, the solid sample, under vacuum, was warmed to room temperature, and its vapor was allowed to enter the previously evacuated cell until a pressure of 10.0 Torr (1.33 kPa) was reached.

Jet-cooled CRD spectra are recorded using a newly constructed vacuum chamber equipped with a pulsed valve assembly. The chamber consists of a six-way cross with 160-mm flanges. A mechanical gate valve separates the chamber from a diffusion pump (Diffstak 100) mounted beneath. The pulsed valve and driver electronics (Jordan TOF, Inc.) afford gas pulses of about 50 $\mu$s duration at 10 Hz. The nozzle is a circular orifice of 0.5 mm diameter, leading to a 1-cm tube also with an inner diameter of 0.5 mm. The tube extension permits placement of the probe laser beam at a distance of only a few nozzle diameters downstream of the gas expansion. The pulsed valve and nozzle are mounted on the top flange of the chamber, so that the free-jet expansion gas is directed into the throat of the diffusion pump and pumped out efficiently.

The optical cavity consists of two high-reflectivity concave mirrors (LGR, $R \geq 0.9995$) with 6-m radii of curvature, mounted at the ends of arms extending from opposite side-flanges of the chamber. The distance between mirrors is 600 mm.

For jet-cooled CRD studies, the dye laser is operated without its main amplifier stage, resulting in pulse energies of 200–300 $\mu$J near 410 nm. The dye laser output beam passes through a spatial filter and is directed into the optical cavity, where it intersects the free-jet expansion perpendicularly. The ringdown decay transient is detected by a photomultiplier module (Hamamatsu H6780) mounted outside the vacuum chamber at the exit mirror.

Liquid acrolein (Acros) was used for the jet-cooled studies without further purification. A cotton ball saturated with a 2-mL portion of the acrolein sample was contained in stainless-steel flow-through filter holder. Helium carrier gas at a pressure of 2 atm entrained the acrolein vapor as it passed through the sample holder and into the stagnation chamber. The sample holder, tubing, stagnation chamber, and nozzle were maintained at a temperature of about 40 °C by resistive heating. Under these expansion conditions, the background pressure in the vacuum chamber was measured to be about 1 × 10\textsuperscript{-5} Torr when the valve operated at 10 Hz.
B. Computational

To conduct geometry optimizations for the $T_1(n, \pi^*)$ state of acrolein, we employed several \textit{ab initio} and density functional theory (DFT) methods.

DFT calculations were performed with the Becke three-parameter Lee-Yang-Parr exchange-correlation hybrid functional (B3LYP)\textsuperscript{24–27} and the Perdew-Burke-Ernzerhof exchange-correlation hybrid functional (PBE0).\textsuperscript{28} Optimized geometries of the $T_1(n, \pi^*)$ state were obtained using both time-dependent density function theory (TD-DFT) and unrestricted density functional theory (UDFT).

The \textit{ab initio} methods used either restricted Hartree-Fock (RHF) or unrestricted Hartree-Fock (UHF) theory to produce singlet or triplet reference wavefunctions, respectively, for analysis via post-HF methods. RHF calculations used configuration interaction including only single excitations (CIS), CIS with a correction for double excitations (CIS(D)), or equation-of-motion coupled-cluster (EOM-EE-CCSD) methods, to obtain the $T_1(n, \pi^*)$ excited state. UHF calculations used second-order Møller-Plesset perturbation theory (UMP2) or coupled-cluster singles doubles (UCCSD) to treat electron correlation.

The UHF triplet reference wavefunction was employed in the multi-configurational complete active space self-consistent field (CASSCF) calculation to obtain the $T_1(n, \pi^*)$ excited state. The active space consisted of $\pi$ bonding and $\pi^*$ antibonding molecular orbitals nominally localized on the C=O and C=C groups, as well as a nonbonding molecular orbital on the oxygen atom. Selection of the active space is consistent with previous CASSCF studies conducted by Reguero,\textsuperscript{7} Roos,\textsuperscript{8} and Godunov.\textsuperscript{11}

All excited-state geometries were calculated under the constraints of $C_s$ point-group symmetry. The calculations employed triple-zeta quality basis sets, specifically the Pople 6-311+G** basis for DFT calculations and the Dunning cc-pVTZ basis set for all \textit{ab initio} calculations. We used the Q-CHEM 4.0 quantum chemistry package\textsuperscript{29} for all calculations except CASSCF geometry optimization, which was performed using GAUSSIAN 09.\textsuperscript{30}

III. RESULTS

A. Overview of spectral features

Figure 3 shows survey CRD spectra recorded under bulk gas conditions at room temperature as well as jet-cooled conditions. Each spectrum shows two intense features, assigned to the two different appreciably populated conformers of acrolein. The work reported here focuses on $s$-$trans$ acrolein, the conformer present in about 95% abundance at room temperature. The spectral features centered near 412 nm mark the $0_0^0$ band of the spin-allowed $S_1(n, \pi^*) \leftarrow S_0$ transition, whereas the 412-nm peaks are due to the spin-forbidden $T_1 \leftarrow S_0$ transition.

Comparison of the two spectra in Fig. 3 shows how the jet expansion has effected rotational and vibrational cooling of the sample. At room temperature, the two origin bands, $T_1 \leftarrow S_0 (s$-$trans$) and $S_1 \leftarrow S_0 (s$-$cis$), show structured rotational contours. The two origin bands are simplified in the jet-cooled spectrum, notably by the diminution of high-$J^*$ sub-band heads appearing in the higher-energy wing of each contour. In particular, the $T_1 \leftarrow S_0 0_0^0$ transition at room temperature has well-defined maxima at 412.4 nm and 412.15 nm (see Fig. 2), but in the jet-cooled spectrum (Fig. 3), the maximum at higher energy is much less intense and more diffuse. As discussed in Secs. III B–III D, this secondary maximum is assigned to overlapping $\Delta K_a = 0$ sub-band heads at low $K_a^*$ but $J^* > 40$. Its suppression in the jet expansion indicates a lowering of the effective rotational temperature.

The jet cooling also eliminates vibronic hot bands, for example, the sequences of the type $X^1\Sigma^+ \rightarrow \Delta v = \pm 1$ and $\pm 2$ branch heads within $\Delta K_a = 0$ sub-bands. (Here, $N$ labels the angular momentum of the rotating nuclear...
Therefore, a precisely characterized fit of the $T_1(n, \pi^*)$ inertial constants is not feasible from a statistical viewpoint. Nonetheless, it has been possible to identify the maxima of eight $\Delta K_a = 0$ sub-bands to a precision of approximately 0.1 cm$^{-1}$. These features, indicated in Fig. 4, form the basis for an optimization procedure that we could implement practically to determine the $T_1(n, \pi^*)$ inertial constants.

We began by assuming that the local maxima observed in the spectrum marked the positions of sub-band heads. To determine rotational quantum numbers for these features, we ran the STROTA program in simulation mode using computed (CASPT2)$^{11}$ inertial constants. From the simulation output, we identified the rotational transition corresponding the head of each sub-band. We used this transition as a proxy for the entire group of nearly coincident unresolved lines observed at the local maximum. The input data for running the program in fitting mode included a list of these transitions for the assigned sub-bands, along with the corresponding wavenumber positions from the CRD spectrum.

Due to the limited spectral resolution and modest size of the list of assigned transitions, our central strategy was to fit just the triplet-state inertial constants by least-squares optimization, while keeping other structural parameters fixed. Specifically, we varied $A^{′′}, B^{′′} \equiv (B^{′} + C^{′})/2$, and $(B^{′} − C^{′})$, considering that the excited-state rotational levels for an asymmetric rotor are explicitly dependent on these quantities. We optimized these parameters with respect to the assigned line positions; we made no attempt to fit intensities within the rotational contour because of likely interference by vibronic hot bands in the observed spectrum.

As the analysis progressed beyond the initial fitting run, we were able to refine the set of quantum numbers assigned to each sub-band maximum to account for the small discrepancy, typically 0.1–0.2 cm$^{-1}$, between the position of the sub-band head and sub-band maximum. These iterative reassignments also took account of the tendency for the $J$' value of the sub-band head to change by a few units as a result of the inertial constants being refined during a run of the program.

The $00^0_{\pi}$ band center, $v_0$, was held fixed at 24247.3 cm$^{-1}$ during the fitting process; this value was determined at the outset by shifting $v_0$ manually until the simulated spectrum optimally matched the observed spectrum in the vicinity of the overlapping $Q$-form branches near 412.4 nm (the band maximum at 24246 cm$^{-1}$).

Other fixed parameters, listed in Table I, include ground-state rotational constants along with centrifugal distortion constants for both the ground and excited states. High-precision inertial constants for the ground state are available from previous microwave spectroscopic work on acrolein.$^{32}$ The centrifugal distortion constants $\Delta J_J$, $\Delta J_K$, and $\Delta J_{JK}$ are also known$^{33}$ for the ground state. We estimated the excited-state distortion constants based on comparison to literature values$^{34}$ available for $s$-trans-glyoxal, O=CH–CH=O, a molecule structurally similar to acrolein.

For polyatomic molecules such as acrolein, the modeling of singlet-triplet rotational structure also requires$^{35}$ the inclusion of spin-spin constants ($\alpha$ and $\beta$) and spin-rotation constants ($\alpha$ and $\delta_0$) for the triplet state. To obtain estimates for these parameters, we relied on previous spectroscopic results...
TABLE I. Molecular constants (cm$^{-1}$) used in the fit of the $T_1 \leftarrow S_0$ $0^0$ rotational contour of acrolein at room temperature.

<table>
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<th>Parameter</th>
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<tr>
<td>$\Delta^{\alpha}_{K^*}$</td>
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Varied parameters$^c$

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<td>$B'$</td>
<td>0.14852(30)</td>
</tr>
<tr>
<td>$C'$</td>
<td>0.13633(30)</td>
</tr>
</tbody>
</table>

$^a$Reference 32.

$^b$Estimated from glyoxal values in Ref. 33.

$^c$Optimized by procedures described in the supplementary material.

$^d$Values in parentheses represent 1σ.

The empirically ascertained linewidth of 0.4 cm$^{-1}$ significantly exceeds the spectral bandwidth of dye laser (0.1 cm$^{-1}$) and the Doppler width (0.04 cm$^{-1}$) expected for acrolein molecules probed in this spectral region at room temperature. Hence, it is homogeneous broadening that contributes most significantly to the observed linewidth. This finding is not surprising, given the fast nonradiative processes identified in previous computational$^7$ and spectroscopic$^{16}$ work on the $(n, \pi^*)$ excited states of acrolein. In our analysis of the jet-cooled CRD spectrum, presented in Sec. III C, we applied a Voigt function to the rotational lines and used the Lorentzian (homogeneous) component to quantify the lifetime broadening associated with $T_1(n, \pi^*) \leftarrow S_0$ rotational lines.

The fitting of $T_1(n, \pi^*)$ inertial constants to the eight assigned sub-band heads resulted in an overall standard deviation of 0.2 cm$^{-1}$, slightly greater than the uncertainty of about 0.1 cm$^{-1}$ associated with the wavenumber assignments of the peak maxima. This quality of fit is reflected in the standard deviations of the inertial constants, shown in Table I. However, the assignment list was limited, so the quoted standard deviations (1σ) likely overestimate confidence in the final fitted results. In particular, discrepancies between the simulated and observed spectra appear in the vicinity of the secondary maximum, where the simulated spectrum does not include the sufficient buildup of intensity. Such discrepancies imply a systematic omission in the fitting model, most likely the neglect of vibronic hot bands that overlap the $0^0$ band at room temperature. Simulation of the jet-cooled spectrum, discussed below, supports this interpretation.

Hot-band congestion could affect the quality of the fit or the confidence in fitted results by distorting the shape of a local maximum observed in the spectrum, so that it does not correspond accurately to its sub-band head assignment. Conservative estimates of uncertainty for the $T_1$ inertial constants are available by considering the results of quantum-chemical calculations, discussed in a later section. Band-contour simulations obtained via these calculations show prominent inconsistencies with the observed spectrum, even for the most computationally expensive methods. Later, we present these simulations and use them to infer rough confidence intervals for the empirically fitted values of the inertial constants.

A final point about the fitting and simulation procedures concerns the determination of $(B - C)$ for the $T_1$ state. This quantity was established solely by the two $K_a = 3$ asymmetry components assigned in the CRD spectrum (see Fig. 4). The other sub-bands, all having greater $K_a$ values, do not have asymmetry splittings that can be resolved under the present experimental conditions. The shortage of data for determining parameters in Table I along with intensity factors described in Section C of the supplementary material.$^{31}$ To produce the simulation, each predicted rotational line was spread out using an input FWHM value and Lorentzian lineshape. For the room-temperature simulation, we used a FWHM of 0.4 cm$^{-1}$; this value was chosen so as to achieve the best agreement with the widths of the numerous resolved features on the extreme red wing of the spectrum. These are separated by about 0.6 cm$^{-1}$, or roughly $4\tilde{B}$; most of the intensity in these features consist of overlapping members of the $O$-form subbranches of the $\Delta K_a = 0$ sub-bands.

![Absorption](image-url)

FIG. 5. Observed (black) and simulated (red) spectra of acrolein as in Fig. 4, but shown on a wider horizontal scale. The simulated spectrum was scaled vertically so that its primary maximum has the same intensity as that of the observed spectrum. The simulation model included only the $0^0$ band of the $T_1(n, \pi^*) \leftarrow S_0$ transition and does not account for the presence of vibronic hot bands, such as the $18^1$ sequence assigned previously.$^{35}$

on 2-cyclopenten-1-one.$^{36}$ Section B of the supplementary material$^{31}$ describes how we ascertained the values of the spin constants as well as the $T_1(n, \pi^*)$ centrifugal distortion constants.

Table I lists the values of $T_1(n, \pi^*)$ inertial constants obtained in the final fitting run of the STROTA program. Figs. 4 and 5 show the band contour simulated by using the
(B − C) leads to exaggerated statistical error in this quantity and possibly systematic error. However, an independent check on (B − C) is possible by considering the inertial defect, \( \Delta \equiv I_{cc} - I_{bb} - I_{aa} \), expected for a measurement of acrolein in its \( T_1(n, \pi^\ast) \) excited state. An analysis of the observed inertial defect is presented in the Appendix and shows that the fitted value of (B − C) is in accord with physical expectation.

C. Analysis of jet-cooled \( 0^0 \) band rotational contour

Fig. 6 shows the jet-cooled CRD spectrum of the \( T_1 \leftarrow S_0 \) \( 0^0 \) band, along with a simulation produced by the STROTA program using the molecular parameters in Table I. For the simulation in Fig. 6, we used a rotational temperature of 63 K. We determined this value by separately recording the \( 0^0 \) origin band of the acrolein \( S_1(n, \pi^\ast) \leftarrow S_0 \) transition under experimental conditions identical to those reported here for the jet-cooled \( T_1(n, \pi^\ast) \leftarrow S_0 \) spectrum. We simulated the \( S_1 \leftarrow S_0 \) \( 0^0 \) band contour, using experimentally reported molecular constants for the \( S_1(n, \pi^\ast) \) state and a rotational linewidth corresponding to the reported natural lifetime of the \( \nu = 0 \) level of the \( S_1(n, \pi^\ast) \) state. We manually varied the rotational temperature until we achieved optimum agreement between simulated and observed \( S_1 \leftarrow S_0 \) contours. This resulted in a temperature of 63 ± 3 K. This value is similar to the rotational temperature of 80 K determined by Paulisse et al.,\(^{16}\) who investigated the jet-cooled \( S_1 \leftarrow S_0 \) spectrum of acrolein.\(^{37}\)

With the rotational temperature under our experimental expansion conditions established, we needed to apply a line-broadening function to the individual predicted rotational transitions in order to produce a simulation. Fig. 6 includes a stick spectrum showing these lines before broadening. The measured CRD spectrum is subject to both homogeneous (lifetime) and inhomogeneous (laser bandwidth) components, leading to a Voigt lineshape for the individual lines. For the Gaussian component, we used a 0.1-cm\(^{-1}\) FWHM corresponding to the known spectral bandwidth of the dye laser output. We varied the Lorentzian FWHM to achieve the best agreement between the simulation and CRD spectrum in the central spike region. We arrived at a value of 0.38 ± 0.05 cm\(^{-1}\) for the Lorentzian FWHM. The uncertainty of ±0.05 cm\(^{-1}\) corresponds to a range of linewidths that produced acceptable simulations when considering rotational temperatures ranging from 60 K to 66 K. In the Discussion section, we use the determined Lorentzian width to infer the natural lifetime of the \( T_1(n, \pi^\ast) \) state.

Outside the central spike region of the jet-cooled spectrum (i.e., in the wings containing \( \Delta \nu = ±1, ±2 \) branches), the agreement between simulated and observed contours is not exact but is qualitatively reasonable. Disagreement here is due mainly to the relatively low S/N of the jet-cooled CRD spectrum. The observed oscillations in the wings are noise and not reproducible rotational structure. This noise coincidentally has the same amplitude as the fine structure seen in the simulation, so the positions of these features, of course, are not expected to agree. This is in contrast to the room-temperature spectrum; note that the vertical scale in Fig. 6 is three orders of magnitude more sensitive than in the room-temperature spectrum shown in Fig. 2. In the latter case, all of the structure is reproducible and much is assignable in terms of sub-band heads.

The jet-cooled CRD spectrum also contains a buildup of intensity in the wings that does not appear in the simulation. A likely explanation for the extra intensity stems from the fact that in a jet-cooled absorption experiment such as CRD, a portion of the resonance signal is generated in the periphery of the expansion, perpendicular to the centerline axis and collinear with the laser beam. The cooling effects in the periphery are reduced relative to that in the denser centerline region. Thus, the CRD probe laser samples regions of the expansion with varying ground-state rotational population distributions. In particular, the warmer regions of the expansion give rise to an intensification of the sub-bands with large values of \( K_a \). The stick spectrum in Fig. 6 illustrates this point by comparing the intensity profiles of the \( K_a = 1 \) and \( K_a = 5 \) sub-bands, assuming a uniform rotational temperature of 63 K along the CRD axis. This was an explicit assumption in creating the simulated contour shown in the upper portion of the figure. However, if portions of the expansion are in fact significantly warmer than 63 K, then in those spatial regions the \( K_a = 5 \) sub-band will intensify relative to \( K_a = 1 \). This
intensification would contribute to the enhanced CRD signal observed in the wings, which is not accounted for in the simulation.

Notwithstanding these anomalous temperature effects, the extra intensity in the jet-cooled spectrum is still greatly suppressed compared to interference observed in the same general region of the room-temperature spectrum. This observation supports the interpretation that the extra intensity at room temperature is due to vibronic hot bands rather than a deficiency associated with the modeling or fitting of the rotational structure.

D. Computational results

Table II shows computed $T_1(n, \pi^*)$ geometrical parameters involving the heavy atoms of acrolein. Also shown are the corresponding inertial constants, for comparison with the values we determined empirically by fitting to the CRD spectroscopic data.

The multiconfigurational methods CASPT2 and CASSCF, along with the unrestricted ground state method UCCSD(T), show the best overall agreement with the fitted triplet-state inertial constants. In general, the tested DFT methods (both time-dependent and unrestricted) provide good agreement with fitted $B$ and $C$ values, but poor agreement with $A$.

The CASPT2 and UCCSD(T) inertial constants are closest to the fitted values, yet they lie outside the 1σ uncertainty ranges obtained from the fitting procedure. Fig. 7 emphasizes this point: it shows the observed $0^0_0$ rotational contour along with simulations produced from the computed CASPT2 and UCCSD(T) inertial constants in conjunction with the fixed molecular parameters listed in Table I. The CASPT2 calculation slightly overestimates the excited-state values of $B$ and $C$; or in other words, it underestimates the decrease in $B$ and $C$ upon excitation to the $T_1(n, \pi^*)$ state. As a consequence, the nearly coincident low-$K_a$ S-branch heads, which comprise the secondary maximum in the contour, occur at higher wavenumber in the simulation than in the observed spectrum. The opposite situation occurs for the UCCSD(T) calculation, which overestimates the decrease in $B$ and $C$ values, causing the simulated secondary maximum to occur at lower wavenumber than observed. Both the CASPT2 and UCCSD(T) calculations overestimate the value of $A$ in the excited state, which would tend to displace the sub-band heads to higher wavenumber; however, that effect is relatively small for the low values of $K_a$ (0–3) represented at the secondary maximum.

These low $K_a$ sub-band positions are dependent on the spin-rotation constants $a$ and $a_0$.22,35 By altering the spin-rotation constants, it is possible to bring the simulations in Fig. 7 into agreement with the observed spectrum in

![Figure 7](image-url)
the region of the secondary maximum. However, for both the CASPT2 and UCCSD(T) simulations, the required adjustment of the spin-rotation constants causes the quantity \((a - a_0)\) to be an order of magnitude larger than those in Table I. The spin-rotation constants, when adjusted in this way, are physically implausible, based on the expected dependence of \((a - a_0)\) on \(B^2\).

In summary, the CASPT2 and UCCSD(T) methods, which represent the highest levels of theory tested, indeed produce excited-state inertial constants that agree best with the empirically fitted values.\(^{39}\) For these methods, the differences between computed and fitted \(B\) and \(C\) values are only 0.0004–0.0006 cm\(^{-1}\), as seen in Table I. These small numerical inaccuracies become visually obvious when the simulated and observed spectra are compared as in Fig. 7. Because these discrepancies are small (around the 2\(\sigma\) values from the fit) yet definitive, they provide very conservative upper bounds for expressing the uncertainty in the fitted \(B\) and \(C\) values. Specifically, we can state with confidence that the empirically fitted values. \(^{39}\) For these methods, the differences between computed and fitted \(B\) and \(C\) values are only 0.0004–0.0006 cm\(^{-1}\), as seen in Table I. These small numerical inaccuracies become visually obvious when the simulated and observed spectra are compared as in Fig. 7. Because these discrepancies are small (around the 2\(\sigma\) values from the fit) yet definitive, they provide very conservative upper bounds for expressing the uncertainty in the fitted \(B\) and \(C\) values. Specifically, we can state with confidence that the empirically fitted values.

\[ A = 1.662 \pm 0.003 \text{ cm}^{-1}. \]

**IV. DISCUSSION**

**A. Computational treatments of the \(T_1(n, \pi^*)\) geometry**

By providing new experimental information and computational results on the \(T_1(n, \pi^*)\) state of acrolein, this work complements several quantum-chemical studies\(^{9,11,13}\) published over the past decade. Much of the prior work has focused on the multi-reference CASPT2 technique. It is considered a “gold standard” for excited-state calculations because it incorporates both dynamical and non-dynamical corrections for electron correlation. However, the CASPT2 method is computationally expensive and therefore impractical for studying molecules much larger than acrolein. Hence, recent studies have considered less expensive alternatives to CASPT2 for calculating excited-state properties, using acrolein and other small organic molecules to provide performance benchmarks.

In 2003, Page and Olivucci\(^9\) used CASPT2 to conduct excited-state geometry optimizations on acrolein and related molecules, including propenoic acid anion and acetone. For the \(S_1(n, \pi^*)\) state of acrolein, they compared the CASPT2 geometry to that obtained by a CASSCF calculation. In 2010, Guido et al.\(^{13}\) used the same set of molecular excited states as Page and Olivucci (including \(S_1(n, \pi^*)\) acrolein) to compare CASPT2 with TD-DFT geometry optimizations. In 2008, Godunov et al.\(^{11}\) characterized the accuracy of CASPT2 and other methods, including CASSCF and EOM-EE-CCSD, by comparing experimental vs. computed inertial constants for the \(S_1(n, \pi^*)\) state of acrolein.

The present study contributes to this body of work by providing \textit{triplet-state} benchmarks to supplement the results of the \(S_1(n, \pi^*)\) investigations noted above. The experimental \(T_1(n, \pi^*)\) inertial constants test the accuracy of previously conducted geometry calculations, particularly the CASPT2 result.\(^{11}\) In addition, the computed \(T_1(n, \pi^*)\) geometries we report here provide comparative assessments of the more economical techniques, as was done previously\(^{9,11,13}\) for the \(S_1(n, \pi^*)\) state.

A simple metric for expressing the accuracy of a given computational method is the Mean of the unsigned Relative Error (MRE, compared to observed values) of the three inertial constants. MRE values are listed in Table II for the methods applied to \(T_1(n, \pi^*)\) acrolein in this work. The CASPT2 calculation has an MRE value of 0.36%, the second-best of all methods tested. The CASSCF calculation produced inertial constants nearly identical to the CASPT2 values, resulting in an MRE of 0.38%. The UCCSD(T) method has a computational expense on par with that of CASPT2; its MRE value, 0.33%, is the best of those considered in this study and similar to that of CASPT2.

For the \(S_1(n, \pi^*)\) state, the CASPT2 method provides the most accurate inertial constants, as determined by Godunov et al.\(^{11}\) The present results show the same outcome for the \(T_1(n, \pi^*)\) state (if the UCCSD(T) results, inapplicable to \(S_1(n, \pi^*)\), are excluded). For the \(S_1\) state, the CASPT2 geometry optimization has an MRE value of 0.09%, compared to 0.9% for CASSCF.\(^{11}\) This comparison shows that in terms of inertial constants, the agreement between the CASSCF and CASPT2 calculation is better for \(T_1\) than \(S_1\).

Notwithstanding the nearly identical CASPT2 and CASSCF inertial constants for the \(T_1\) state, the two methods produce substantially differing geometrical parameters, as seen in Table II. The CASSCF calculation predicts significantly longer C\(\equiv\)C and C\(\equiv\)O bonds than CASPT2, and a significantly shorter C\(\equiv\)C bond than CASPT2. In other words, the CASSCF calculation, compared to CASPT2, exaggerates the effect of occupancy of the \(\pi^*\) orbital. This orbital has antibonding character (i.e., nodes) located at the C\(\equiv\)O and C\(\equiv\)C bonds, and bonding character at the C\(\equiv\)C bond. Therefore, the \(\pi^* \rightarrow \pi \) excitation causes the C\(\equiv\)C and C\(\equiv\)O bond orders to decrease from their nominal values of two, whereas the C\(\equiv\)C bond order increases. The amplification of these bond-order changes in CASSCF calculations, compared to CASPT2, has been also been observed by Page and Olivucci\(^9\) for the \(S_1(n, \pi^*)\) state of acrolein.

It is interesting to note that the UHF calculation presented here for the \(T_1(n, \pi^*)\) state produces geometrical parameters that are nearly identical to the CASSCF results. Neither of these methods includes corrections for dynamical electron correlation. The UCCSD(T) calculation includes this correction at a high level, and it predicts a less severe lengthening of the C\(\equiv\)O bond and shortening of the C\(\equiv\)C bond than the UHF calculation.

In summary, four of the calculations considered—CASPT2, CASSCF, UCCSD(T), and UHF—produce nearly identical, and very accurate, sets of inertial constants for the \(T_1(n, \pi^*)\) state. However, two of the methods, CASSCF and UHF, lack a correction for dynamical correlation. These two
methods predict exaggerated bond-order changes upon excitation compared to the high-level CASPT2 and UCCSD(T) calculations.

In addition to the ab initio investigations described above, DFT methods have been used to characterize bond lengths for singlet states, both ground and excited. In their 2010 investigation of acrolein and related small chromophores, Guido et al. concluded that both DFT (when applied to the ground state) and TD-DFT (for \( S_1 \)) present an overly “localized” bonding picture, wherein the lengths of nominally double bonds are underestimated and those of single bonds are overestimated by comparison to CASPT2. We find this to be the case also for the \( T_1(n, \pi^*) \) state of acrolein (see Table II), although the contrast between TD-DFT and CASPT2 results is less than for \( S_1(n, \pi^*) \). For example, the present TD-B3LYP and TD-PBE0 calculations of the \( T_1(n, \pi^*) \) state predict C–O bonds that are respectively 0.019 and 0.032 Å shorter than in the CASPT2 calculation; Guido et al. found these differences to be 0.052 and 0.061 Å for \( S_1(n, \pi^*) \).\(^{40}\)

The DFT calculations here generally show only moderate bond-length deviations from CASPT2, and the DFT methods lead to very accurate \( B \) and \( C \) rotational constants for the \( T_1(n, \pi^*) \) state. Among the TD-DFT and UDFT methods in Table II, the average unsigned relative error for \( B \) and \( C \) (compared to observed values) is only 0.39%. The UPBE0 method is particularly successful in this regard, with an error of 0.21%. This result from an unrestricted (i.e., ground-state) DFT technique is consistent with an observation of Guido et al.—that DFT calculates the C=O bond length more accurately for \( S_0 \) than TD-DFT does when applied to \( S_1 \).\(^{13}\)

In the present \( T_1(n, \pi^*) \) calculations, the DFT \( A \) constants are much less accurate than the \( B \) and \( C \) values. The \( A \) value is overestimated in each of the calculations in Table II, with an average deviation of 2.8% compared to observed. At least in part, these errors are related to the prediction of how much the C–C=O and C=C–C bond angles open up as a result of \( \pi^* \leftarrow n \) excitation. The DFT calculations appear to overestimate these angles in the \( T_1 \) state, causing the molecular geometry to be closer to linear and increasing the \( A \) constant. Similar effects are observed\(^ {13} \) for TD-DFT calculations of the \( S_1(n, \pi^*) \) state.

**B. Lifetime of the \( T_1(n, \pi^*) \) state**

As discussed above, the best-fitting simulation of the \( 0_0^0 \) band contour in the jet-cooled \( T_1(n, \pi^*) \leftarrow S_0 \) spectrum leads to a Lorentzian (homogeneous) linewidth of 0.38 ± 0.05 cm\(^{-1} \) for individual vibronic transitions. This corresponds to a natural lifetime of \( \tau = 14 \pm 2 \) ps for the \( v = 0 \) level of the triplet excited state, from the relationship

\[
\tau = \frac{1}{2\pi \Gamma}
\]

The inferred lifetime of 14 ps is dominated completely by nonradiative decay processes, as the typical radiative (phosphorescence) decay rate for a \( ^3(n, \pi) \) state corresponds to a lifetime on the order of 1 ms.\(^ {41} \)

By studying the \( S_1(n, \pi^*) \leftarrow S_0 \ 0_0^0 \) band under similar jet-cooled conditions to those reported here for the \( T_1(n, \pi^*) \leftarrow S_0 \) transition, Paulisse et al.\(^ {16} \) found the \( S_1(n, \pi^*) \) lifetime to be in the range 1.8–2.1 ps. This lifetime is about one order of magnitude shorter than we have found for the \( T_1(n, \pi^*) \) state.

The CASSCF computational study of Reguero et al.\(^ {7} \) can help to rationalize these very short lifetimes, as well as explain the difference in magnitude between the \( S_1(n, \pi^*) \) and \( T_1(n, \pi^*) \) values. The calculations indicate that the planar global minimum of each state plays a critical role in the solution-phase photochemical behavior of acrolein. Because of the importance of these planar minima, Reguero et al.\(^ {7} \) exhaustively characterized the potential surface of each state, along with that of \( T_2(\pi, \pi^*) \), in planar regions of the acrolein coordinate space. They found a surface crossing between \( S_1(n, \pi^*) \) and \( T_2(\pi, \pi^*) \) near the \( S_1(n, \pi^*) \) minimum; they also found a conical intersection between \( T_1(n, \pi^*) \) and \( T_2(\pi, \pi^*) \) near the \( T_1(n, \pi^*) \) minimum. According to the calculations, both of these crossings with \( T_2 \) occur within about 5 kcal/mol (2000 cm\(^{-1} \)) of the respective \( (n, \pi^*) \) minima.

Because of these surface intersections, the exit out of the \( S_1 \) or \( T_1 \) minimum can be extremely rapid in solution, according to the calculations of Reguero et al.\(^ {7} \). In the present spectroscopic experiments, with a gas-phase sample under isolated-molecule conditions, the photophysical dynamics cannot be expected to be the same as characterized by Reguero,\(^ {7} \) as no solvent reservoir is present to facilitate the movement of the acrolein system about its potential-energy landscape. Nonetheless, for both \( S_1(n, \pi^*) \) and \( T_1(n, \pi^*) \), the proximity of surface intersections with \( T_2(\pi, \pi^*) \) indicates that the Franck-Condon factors for nonradiative transitions to \( T_2 \) should be large, which would lead to short lifetimes even under the present isolated-molecule conditions.

Of course, with the data currently available, it is not possible to quantify the Franck-Condon factors or the electronic matrix elements for the interactions between \( T_2(\pi, \pi^*) \) and \( T_1(n, \pi^*) \) or \( S_1(n, \pi^*) \). However, because the \( v = 0 \) level of \( S_1 \) is 1600 cm\(^{-1} \) higher than that of \( T_1 \), the density of \( T_2(\pi, \pi^*) \) background states is significantly greater near \( S_1 \) than \( T_1 \). This would lead to a faster nonradiative decay rate for \( S_1 \) (as observed), if other factors were equal.

**V. CONCLUSIONS**

In this paper, we have analyzed cavity ringdown absorption spectra to obtain structural and lifetime information for the \( v = 0 \) level of acrolein in its \( T_1(n, \pi^*) \) state. We used empirically fitted values of the \( T_1 \) inertial constants to test the accuracy of a variety of computational methods. We find that the CASPT2 method, considered a “gold standard” for excited-state calculations, does produce inertial constants that are among the most accurate of those obtained here. However, the benchmarking process has revealed several caveats:

1. The UCCSD(T) technique produces \( T_1(n, \pi^*) \) inertial constants that are slightly more accurate than the CASPT2 results, by comparison to fitted values.
2. When the CASPT2 or UCCSD(T) inertial constants are used to simulate the \( 0_0^0 \) band of the \( T_1 \leftarrow S_0 \) spectrum, the simulated and observed band contours have
noticeable discrepancies—even though the computed and fitted inertial constants differ by less than 0.4% on average.

3. The empirically fitted inertial constants are subject to imprecision associated with spectral congestion at room temperature; however, the clear discrepancies between simulated and observed band contours for the computational methods above have helped us to determine an upper limit for the uncertainty range of the fitted inertial constants.

These outcomes underscore the value of spectroscopy for testing the computational methods quantitatively—even those methods, such as CASPT2 and UCCSD(T), that represent the highest available levels of theory. Although the present spectroscopic data set is insufficient for determining individual geometrical parameters such as bond lengths and angles, it has gauged the level of accuracy of the CASPT2 and UCCSD(T) calculations via comparison of inertial constants. Such validation is essential when the high-level techniques are used to benchmark less expensive methods, as we and others have done.

In future work, we plan to conduct further spectroscopic studies of the $T_1(n, \pi^*) \leftarrow S_0$ transition of acrolein, by recording and fitting the $0^0_0$ bands of isotopically substituted derivatives. These experiments will allow us to determine the $T_1(n, \pi^*)$ bond lengths and angles experimentally. We also plan to record the jet-cooled spectra of acrolein and its isotopomers using a slit nozzle rather than a pinhole. The planar expansion from a slit source will lead to an improvement in SNR by increasing both the effective absorption pathlength and the molecular density at a given downstream distance. The ensuing analyses of the $0^0_0$ rotational contours should provide fitted inertial constants with narrower confidence intervals than we have reported here. These planned experiments will provide an increasingly precise set of benchmarks for testing the computational methods.

Finally, we plan to record the spectra of $v' > 0$ vibronic bands of acrolein within the $T_1 \leftarrow S_0$ system in order to analyze triplet-state lifetimes at higher levels of vibrational excitation. This will provide further insight on nonradiative decay channels available to the $T_1(n, \pi^*)$ state.

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**APPENDIX: ANALYSIS OF $T_1(n, \pi^*)$ INERTIAL DEFECT**

For a molecule having a planar equilibrium structure, its inertial defect $\Delta \equiv I_{cc} - I_{sb} - I_{aa}$ would be zero if the molecule did not undergo zero-point motion. Zero-point vibration in the molecular plane leads to a slightly positive $\Delta$ experimental inertial defect $\Delta_0 = \frac{\hbar^2}{2} (1/C - 1/B - 1/A)$, where $A \equiv \frac{B}{2} (I_{aa}^{-1})$, etc. The positive-signed outcome for $\Delta_0$, traceable to vibrational averaging effects, is observed for molecules that do not undergo large-amplitude out-of-plane motion.32 For example, malonaldehyde, a planar molecule with strong intramolecular hydrogen bonding, has a measured inertial defect of $\Delta_0 = +0.1026$ amu-Å$^2$. However, acyclic molecules having low-frequency skeletal torsion (out-of-plane) modes typically show negative values of $\Delta_0$ in their ground electronic states. Examples are $s$-trans-acrolein, $s$-trans-glyoxal, and $s$-cis-glyoxal. For these molecules, with torsion fundamentals of 158, 127, and 108 cm$^{-1}$, respectively, the $S_0$ inertial defects are $\Delta_0 = -0.0212$, $-0.0066$, and $-0.1286$ amu-Å$^2$.

For each of these molecules, the torsion frequency in the $(n, \pi^*)$ excited state is higher than in the ground state because the bond order of the central C–C bond increases upon excitation. The $S_0(n, \pi^*)$ state of $s$-trans-glyoxal has a torsion fundamental of 232 cm$^{-1}$, an increase of 105 cm$^{-1}$ compared to the ground-state frequency, and the measured inertial defect becomes more positive by 0.094 amu-Å$^2$, attaining a value of $\Delta_0 = +0.028$ amu-Å$^2$. Glyoxal follows the general trend for more rigidly planar molecular species to have more positive inertial defects. Assuming acrolein also follows this trend, and given its increase in torsion frequency from 158 to 216 cm$^{-1}$ upon $T_1(n, \pi^*) \leftarrow S_0$ excitation, one would expect the inertial defect in the $T_1$ state to be more positive than the ground-state value of $\Delta_0 = -0.0212$ amu-Å$^2$. The present spectroscopic results are in accord with this expectation. The $T_1(n, \pi^*)$ inertial constants listed in Table I yield an inertial defect of $\Delta_0 = +0.008$ amu-Å$^2$ (or $+0.01$ amu-Å$^2$ taking into account the decimal precision of the current experiment). Thus, the observed inertial defect is physically plausible.

The experimental inertial defect, $\Delta_0 = +0.01$ amu-Å$^2$, is also uniquely compatible with features in the CRD spectrum. Fig. 8 shows simulations of the $T_1(n, \pi^*) \leftarrow S_0$ contour in region of the $K_a = 3$ sub-band heads. Each simulation employs a different value of $\Delta_0$, including the one (in green) corresponding to our least-squares fitting results. All simulations were produced using the excited-state $A$ and $\tilde{B}$ constants from Table I, but each considers a different possibility for $(B - C)$, a quantity subject to exaggerated experimental uncertainty due to the limited resolution of the spectrum. For two of the simulations, the values of $(B - C)$ were constructed from hypothetical, but physically plausible, predictions of $\Delta_0$ for the $T_1(n, \pi^*)$ state. These simulations correspond to the $\Delta_0$ choices closest to $+0.01$ amu-Å$^2$. Finally, considered in Fig. 8 are three $(B - C)$ values corresponding to implausible choices for $\Delta_0$.

The empirically fitted contour and the ones adjacent to it show a similar and acceptable level of qualitative agreement with the CRD spectrum in the $K_a = 3$ region; however,
FIG. 8. Top two traces: room-temperature CRD spectrum, as in Fig. 4, recorded at a dye-laser resolution of 0.1 cm\(^{-1}\), and spectrum recorded at higher resolution (0.03 cm\(^{-1}\)) by using the dye laser’s intracavity etalon accessory. Lower six traces: spectra simulated at 0.03-cm\(^{-1}\) resolution. The simulations employed the fixed constants in Table I, along with fitted values of \(A'\) and \(B'\). For each simulation, the quantity \((B' - C')\) was constructed by using the indicated value of \(\Delta_0\). The inertial defects, in units of amu-Å\(^2\), are those of \(S_0\) malonaldehyde \((+0.10), S_1\) s-trans-glyoxal \((+0.028), T_1\) acrolein \((+0.01, as determined in this work), S_2\) acrolein \((-0.021), S_3\) s-trans-glyoxal \((-0.066), and S_0\) s-cis-glyoxal \((-0.13). The inertial defects of \(S_0\) malonaldehyde (a species with restricted out-of-plane vibration) and \(S_0\) s-trans- and s-cis-glyoxal (species with exaggerated out-of-plane vibration) are physically implausible for \(T_1\) acrolein.

the three simulations corresponding to unrealistic values of \(\Delta_0\) deviate substantially from the CRD assignments. Thus, although the CRD spectrum is congested in this region (most likely due to vibronic hot bands) it still has sufficient resolved detail to discriminate between physically suitable and unsuitable values of \(\Delta_0\). Therefore, it can discriminate between accurate and inaccurate values of \((B - C)\), if it is assumed that \(A\) and \(B\) have been determined correctly via the fit in other regions of the spectrum. This conclusion adds confidence to the value of \((B - C)\) determined by least-squares fitting and represented in the simulation shown in green in Fig. 8.

31. See the supplementary material at http://dx.doi.org/10.1063/1.4789791 for a discussion of rotational line patterns, as well as estimation of parameters held fixed in the fitting procedure and intensity factors used to simulate the \(T_1(n, \pi^\ast) \leftrightarrow S_0\) spectrum.
37. A rotational temperature of 63 K is relatively warm for a free-jet expansion of a medium-sized molecule such as acrolein entrained in helium. In the present experiment, it was necessary to place the laser probe only a few nozzle diameters downstream of the nozzle, in an incompletely cooled region of the expansion, because the resonance signal became too weak to detect at larger downstream distances.
39. The inertial constants obtained from quantum-chemical calculations correspond to the equilibrium geometry of the \(T_1(n, \pi^\ast)\) excited state, whereas the spectroscopically determined inertial constants contain the effects of vibrational averaging due to zero-point motion. Therefore, in comparing computed vs. experimental inertial constants, it is technically necessary to modify the latter so that they reflect the equilibrium, rather than \(v = 0\) geometry. In the \(T_1\) excited state, the in-plane bending vibrations have large amplitudes and lead to the most significant vibrational averaging effects. (The contribution due to out-of-plane torsion is mitigated by the increase in \(C \sim C\) bond order upon \(T_1(n, \pi^\ast)\) excitation.) Specifically, the bending vibrations, due to anharmonicity, tend to increase the angles within the heavy-atom framework, straightening out the molecule along the \(a\) axis and causing the observed \(A\) constant \((v = 0)\) to be slightly larger than it would be in the absence of zero-point motion; \(B\) and \(C\) are relatively unaffected. (Purly, mathematical effects of vibrational averaging; i.e., arising from the fact that \(I_{zz}^{\text{°}} \neq I_{oo}^{-1}\), also cause the observed \(A\) constant to be larger than it was at equilibrium.) Thus, the modification necessary for comparison between experimental and computed inertial constants is to revise the experimental \(A\) constant downwards of 1.662 \(\text{cm}^{-1}\). Such a modification would widen the discrepancies between experimental and computed \(A\) values in Table II. A way to estimate the magnitude of the effect is to calculate the value of \(A\) that would produce an inertial defect of zero (as is necessary for the planar equilibrium geometry) when the observed \(B\) and \(C\) constants are used. This results in \(A = 1.659 \text{ cm}^{-1}\).
It is possible that the differences in TD-DFT performance for $S_1(n, \pi^*)$ vs. $T_1(n, \pi^*)$ are attributable in part to the difference in basis set used for the two calculations. Guido et al. used the 6-31+G* basis set for the $S_1(n, \pi^*)$ calculation, whereas we have used the 6-311+G** basis set for the $T_1(n, \pi^*)$ calculation.


The torsion frequency of acrolein in its $S_1(n, \pi^*)$ state is $250 \text{ cm}^{-1}$, compared to the ground-state value of $158 \text{ cm}^{-1}$. Therefore, the inertial defect in the $S_1(n, \pi^*)$ state is expected to be more positive than in the ground state. The known inertial constants for the $S_1(n, \pi^*)$ state bear this out, yielding a value of $\Delta q = 0.0 \text{ amu-Å}^2$; however, because the decimal precision does not permit informative comparison with the other values represented in Fig. 8, the result for $S_1(n, \pi^*)$ acrolein is not included in the figure.