The vibrationless $\tilde{A} \rightarrow \tilde{X}$ transition of the jet-cooled deuterated methyl peroxy radical $\text{CD}_3\text{O}_2$ by cavity ringdown spectroscopy

Shenghai Wu, Patrick Dupré, Patrick Rupper, and Terry A. Miller

Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210, USA

(Received 14 September 2007; accepted 3 October 2007; published online 12 December 2007)

The nearly rotationally resolved spectrum of the $\tilde{A}^2A' \rightarrow \tilde{X}^2A'' 0_0^0$ transition of perdeutero methyl peroxy near 1.35 \(\mu\)m has been studied via pulsed cavity ringdown spectroscopy. Albeit, this is a weak transition, it is possible to observe the spectrum under jet-cooled conditions (\(\approx 15\) K) by combining a source of narrow-bandwidth radiation (\(\approx 250\) MHz) with a supersonic slit-jet expansion incorporating an electric discharge. The near infrared radiation was obtained by using stimulated Raman scattering and a pulsed, nearly Fourier-transform-limited Ti:sapphire amplifier seeded by a scanable cw Ti:sapphire ring laser. The experimental spectrum has been fitted using a model Hamiltonian that includes the rigid body rotation of an asymmetric top and the spin-rotation interaction. An excellent quality fit was obtained resulting in the determination of 15 molecular parameters characterizing the $\tilde{A}$ and $\tilde{X}$ states. Other results reported for $\text{CD}_3\text{O}_2$ include an estimate of the radical concentration and the vibronic transition dipole from the observed absorption intensities. Details about the spectral linewidths are also discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2802202]

I. INTRODUCTION

The crucial role of peroxy radicals (RO$_2$) in low temperature combustion and atmospheric chemistry has been intensively discussed in previous papers\(^{1-4}\) and references therein. Moreover, their potentially important role in biochemistry has also been recognized,\(^{5-7}\) where their involvement in lipid peroxidation is considered to be a potentially important source of carcinogenesis, tandem mutations, and premutagenic DNA damage; although, the detailed mechanisms are not well understood. Spectroscopic diagnostics\(^8\) are the most straightforward approaches to detect and quantify radical intermediates and thereby explore the mechanisms and kinetics of their reactions. Peroxy radicals exhibit a strong $\tilde{B} \rightarrow \tilde{X}$ electronic absorption transition in the UV which is useful for their detection. However, this transition has the major disadvantage of being intrinsically broad and structureless because of the dissociative nature of the $\tilde{B}$ state,\(^{1,9,10}\) particularly limiting the specificity of the spectroscopic diagnostic. A spectroscopic alternative to the $\tilde{B} \rightarrow \tilde{X}$ transition is the $\tilde{A} \rightarrow \tilde{X}$ transition which is located in the near infrared (NIR) region of the spectrum.\(^{11}\) However, this transition suffers from a small absorption cross section ($10^{-10} - 10^{-7}$ smaller than the UV one) and requires sensitive detection techniques. Recently, this transition has been the object of spectroscopic studies, thanks to the advent of relatively new absorption-based techniques such as cavity ringdown spectroscopy (CRDS).\(^{12}\) Pushkarsky et al. published\(^{13}\) the first pulsed, room temperature CRDS spectrum of the $\tilde{A} \rightarrow \tilde{X}$ transition obtained for the C(H/D)$_2$O$_3$ and C$_2$H$_5$O$_2$ radicals with others subsequently\(^{14}\) utilizing cw-CRDS for their detection.

Recent CRDS experiments\(^{13,15-22}\) on various alkyl peroxy radicals have demonstrated the sharp, structured $\tilde{A} \rightarrow \tilde{X}$ spectra that can be used to distinguish among different R groups, and even among different isomers and conformers of the same RO$_2$ radical. However, they have been only able to resolve rotational contours because of the congestion caused by the overlap of different rotational lines of the same, and also different conformers at room temperature. Due to the rotational congestion of the room temperature spectrum, jet cooling is an appealing technique to improve the resolution, and Fu et al.\(^{23}\) recently obtained the first jet-cooled NIR spectrum of CH$_3$O$_2$ in a time of flight mass spectrometric experiment but with relatively low resolution due to the bandwidth of their laser source.

In order to obtain the maximum information available from the spectra, it would be desirable to have rotationally and spin-rotationally resolved spectra, as these would provide molecular parameters to characterize the radicals and to benchmark quantum chemistry calculations for them. Such analyses would directly identify the spectra of different isomers and conformers rather than relying on inferences based upon quantum chemistry calculations. An apparatus that combines a highly sensitive absorption technique, a high resolution laser source, and a cold molecule-radical source has recently been developed in our group and already proven its capability for such detailed spectroscopic investigations.\(^{24}\) In this paper, we report the use of this apparatus to obtain the jet-cooled, nearly rotationally resolved spectrum of the perdeutero methyl peroxy radical.

The apparatus has been improved and refined since the last report,\(^{24}\) and we discuss these changes in some detail in Sec. II. Sec. III overviews the basic theory involved in the analysis of the observed spectra of CD$_3$O$_2$. In Sec. IV, we
describe the spectral analysis and discuss the results therefrom which include a set of 15 molecular parameters describing the \( \tilde{X} \) and \( \tilde{A} \) states of the radical as well as estimates of its concentration and transition dipole, and observations about the widths of the lines.

To conclude this introduction, it is worthwhile commenting on why we are presenting here the analyses of the CD\(_3\)O\(_2\), and not the CH\(_3\)O\(_2\), spectra. Although the latter’s spectrum has also been fully recorded and measured, it has yet to be completely analyzed. In recent works\(^{23,26} \) on the room temperature spectra of CH\(_3\)O\(_2\) and CD\(_3\)O\(_2\), we discussed the importance of methyl torsion and predicted tunneling splittings in the vibrationless level of CD\(_3\)O\(_2\) to be \( \approx 100–200 \) MHz, while for CH\(_3\)O\(_2\), the corresponding splittings were \( \approx 2.0–3.0 \) GHz. Given our experimental resolution, it is likely that effects of the torsional motion in CD\(_3\)O\(_2\) will be smaller than our linewidth, while in CH\(_3\)O\(_2\), splittings greater than the linewidth, and comparable to spin-rotational splittings, will be present. This naturally gives rise to a more complex and congested spectrum and its more complicated analysis is ongoing.

II. EXPERIMENT

The previously reported experimental setup\(^{24} \) has been partially redesigned to increase and stabilize the concentration of transient species, particularly peroxy radicals, produced as well as to maximize their cooling. In addition, we have worked to improve the sensitivity of the CRDS spectrometer. In the following, we discuss separately three different aspects of the experiment (see Fig. 1 of Ref. 24 for a schematic picture of the experimental setup): the CRDS spectrometer, radical production and cooling, and finally, data acquisition, calibration, etc.

A. CRDS spectrometer

The laser system for the spectrometer has been described in Ref. 27. Briefly, this homemade source delivers nearly Fourier-transform-limited, \( \approx 15 \) ns pulses in the Ti:sapphire (Ti:Sa) spectral range with pulse energies up to 100 mJ. It operates via the amplification of a cw beam issued from a Ti:Sa ring laser (Coherent 899-21). The amplification occurs by quadruple pumping of each end of two Ti:Sa rods (located inside an optical cavity) with a frequency doubled, 20 Hz Nd:YAG (yttrium aluminium garnet) laser (Lab-170 Spectra Physics). The locking of this cavity to the Ti:Sa ring frequency is based on the ramp-lock-fire technique and is accomplished by a digital signal processor. The amplifying cavity behaves as a slave cavity of the single mode tunable ring cavity whose wavelength control is determined by the usual Autoscan control box of the 899-21 system.

The spectral linewidth of the amplifier depends primarily on the YAG pump energy and has been measured from \( \approx 8 \) to \( \approx 30 \) MHz [full width at half maximum (FWHM)], thereby constituting an almost ideal source for the nonlinear generation of radiation for high resolution spectroscopy. In this work, NIR radiation has been obtained by stimulated Raman scattering (SRS) inside a stainless steel cell (\( \approx 1 \) m long) whose windows are at the Brewster angle and which is filled with gaseous hydrogen whose pressure can be adjusted from 0 to 20 atm and is typically set to \( \approx 13 \) atm. A slight collimation of the incoming beam through a lens (\( f \approx 0.8 \) m) is necessary to optimize the SRS. The first Stokes SRS output used in these experiments is pressure and incoming energy dependent. The spectral broadening of the SRS is not very well quantified but its estimated\(^{24} \) linewidth in the 1.3–1.4 \( \mu \)m range is \( \approx 250 \) MHz (FWHM). Dispersion of the output beam is accomplished by two Pellin-Broca prisms allowing only the first Stokes SRS radiation to enter the CRDS cavity. The output energy of the beam can be up to a few millijoules; however, typically less than half a millijoule is required.

The CRDS high finesse cavity consists of two high reflectors (from Los Gatos or Advanced Thin Films) mounted on the arms of an evacuated chamber (0.67 m long). Mirror damage from the reactive chemicals in the chamber is avoided by flowing inert gas in front of each mirror. These additional inlets to the chamber can also be used to introduce other gases, such as water vapor, for calibration purposes.

B. Radical production and cooling

Given the small oscillator strength of the \( \tilde{A} - \tilde{X} \) transition and the relative insensitivity of any absorption technique, even CRDS, it is incumbent that the peroxy radical’s concentration be maximized while its temperature be minimized, to the extent that it is simultaneously possible. In ambient temperature CRDS works\(^{13,25} \) on methyl peroxy radicals with slow flow cells, the radicals have been produced by photolysis. However, the rapid flow of photolysis products in a supersonic jet through the sampling region precludes sample time durations compatible with the CRDS time scale (\( \approx 100 \) \( \mu \)s).

For this reason, we have chosen to use a discharge source, which can be readily sustained for \( \approx 500 \) \( \mu \)s. Figure 1 shows the details of our transverse discharge geometry. Our apparatus has evolved from an earlier longitudinal version,\(^{27} \) which was heavily based on the designs of Lovejoy and Nesbitt,\(^{28} \) and Liu et al.,\(^{29} \) and has been subsequently implemented and modeled in several other works.\(^{30–32} \) We adopted the present transverse design based on a number of empirical tests. Our experience is that the transverse design gives a modest improvement in \( S/N \) compared to the longitudinal discharge (at least as implemented in our laboratory) and a significant improvement in long-term stability. It also has the advantage of localizing the discharge inside a small volume defined by the two electrodes, thereby avoiding the leaking of the plasma into the chamber beyond the throat of the expansion.

The opening of the slit (1 mm \( \times \) 5 cm) is accomplished by two modified General Valve devices (Parker, series 9) activated by General Valve drivers (Iota), with an opening time of \( \approx 1 \) ms. The plasma channel length (\( \approx 9 \) mm) and the spacing (\( \approx 1 \) mm) between the two stainless steel electrodes are not critical parameters, but the electrode surface finishing is a key point for the stability of the plasma. Theoretically, a longer channel should help the chemical processes by in-
The connection is via a fast switch and adjustable high voltage power supply. The channel is defined by the two Macor shoes which isolate the two polished stainless steel electrode plates than the discharge channel and is closed by a Viton poppet mounted on a light aluminum armature which is itself attached to the armatures of two Parker valve actuators.

The plasma is produced by applying a time controlled electric field between the two electrodes during the opening time of the slit. We used several kinds of electric fields: quasicontinuous (dc), radio frequency (rf), and a combination of both. (1) For the dc discharge, the current is delivered to the electrodes from two 50 $\mu$F capacitors, charged by an adjustable high voltage power supply ($\leq$3 kV, Spellman). The connection is via a fast switch (DEI) through a ballast resistor which can be varied from 0.5 to 5 k $\Omega$ giving a typical plasma voltage drop of $\approx$500 V. The current is monitored by a Hall effect sensor and a maximum current of 1 A is available, but 300–400 mA is typically used. (2) For the rf discharge, a rf voltage is delivered by a digital synthesizer (HP/Agilent) whose frequency can be adjusted from 0 to 20 MHz and whose amplitude modulation input was utilized to control the discharge duration. This rf voltage is amplified by an ENI rf amplifier (which can deliver up to 100 W on a 50 $\Omega$ resistive load) and requires an impedance matching network (Heathkit). (3) For dc and rf combination, to increase the available energy to the discharge, both power supplies were combined through a homemade capacitor/inductance coupler network.

Data have been obtained by using each of these arrangements according to different optimization criteria such as radical production and discharge stability, which are critical for reaching the lowest noise in the CRDS spectrometer. The discharge stability depends on the precursor seeding rate, on the current through the discharge, and on the status of the electrode surface. For example, when using methyl iodide as a precursor, we quickly observe a deposit of iodine on both electrodes that limits the duration of the experiment and requires cleaning. This iodine deposit is much less pronounced when using a rf discharge. Minimizing the discharge duration is another way to improve the discharge stability. The best signal to noise ratios ($S/N$) have been obtained by using only the dc source. However, maximum peroxy production has been obtained by combining the dc and rf sources.

The chemistry in the channel before the expansion was modeled by the set of reactions and rate constants given in Table I. A simple routine solved the coupled differential equations and predicted species concentration as a function of time (or point downstream using the carrier gas flow velocity). As described in Ref. 24, our CRDS system can also be operated in the mid-IR where vibrational absorptions of a number of the key species (several with known cross sections) can be observed. These observations confirmed that this model was, at worst, a reasonable description of the chemistry. An interplay of model predictions and empirical adjustments optimized the production of radical species such as CH$_3$ and CH$_3$O$_2$.

![Figure 1](image.png)

**FIG. 1.** (Color online) Slit nozzle expansion for radical production utilizing the transverse discharge arrangement. The width, typically 0.8 mm, of the channel is defined by the two Macor shoes (MS) and the teflon spacers (TF) which isolate the two polished stainless steel electrode plates (EP) with a 5 cm $\times$ 5 mm cross section. The valve slit (1 mm wide) is slightly larger than the discharge channel and is closed by a Viton poppet (VP) mounted on a light aluminum armature which is itself attached to the armatures of two Parker valve actuators.

### Table I. The main chemical reactions in the discharge of CH$_3$I with O$_2$ (reactions 3–7) and without O$_2$ (reactions 1 and 2) and their rate constants.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>Rate (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$I $\rightarrow$ CH$_3$+I</td>
<td>$k_0^3$=1.17$\times$10$^{-24}$($T$/298 K)$^{-3.75}$e$^{-894 K/T}$ cm$^3$ molecule$^{-1}$</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>2 CH$_3$ $\rightarrow$ C$_2$H$_6$</td>
<td>$k_0^2$=7.42$\times$10$^{11}$($T$/298 K)$^{-1.69}$e$^{-88 K/T}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>O$_2$ $\rightarrow$ 2 O</td>
<td>$k_0^5$=1.0$\times$10$^{-30}$($T$/300)$^{-1.3}$ cm$^3$ molecule$^{-1}$</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$+O$_2$ $\rightarrow$ CH$_3$O$_2$</td>
<td>$k_0^4$=1.2$\times$10$^{-12}$($T$/300)$^{1/2}$</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$+O $\rightarrow$ H$_2$CO+H</td>
<td>$k_0^5$=2.4$\times$10$^{-10}$e$^{-202 K/T}$</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$+CH$_3$O$_2$ $\rightarrow$ 2 CH$_3$O</td>
<td>$k_0^6$=8.7$\times$10$^{-11}$e$^{-186 K/T}$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2 CH$_3$O$_2$ $\rightarrow$ products</td>
<td>$k_0^7$=9.1$\times$10$^{-14}$e$^{116 K/T}$</td>
<td></td>
</tr>
</tbody>
</table>
Typically, CD$_3$I and $\approx$10% O$_2$ in “first run” neon (approximately 75% of Ne and 25% of He) were used for the present study. Good control of the mole fractions of these species is required to optimize the discharge expansion. Important adjustable parameters are the backing pressure (<1 atm) and the rates of seeding of both species (CD$_3$I and O$_2$). These are optimized to obtain a high radical density and efficient cooling. The seeding rate of the methyl iodide is a key point for getting an efficient cooling, as excess CD$_3$I leads to higher radical rotational temperatures. Its seeding rate is reproducibly controlled by the temperature of the bath surrounding the precursor container. A temperature range from $-35$ to $-55$ °C has been commonly used for the present study. Assuming that the temperature is the only parameter controlling the vapor pressure above the liquid sample, this yields CD$_3$I partial pressures in the range of 20 to 5 torr at equilibrium. However, the assumption of equilibrium is questionable as the bubbling of the carrier gas through the liquid increases the seeding rate for a given bath temperature compared to a simple overflow. The absolute seeding rate is, therefore, only approximately known, but we can estimate it as $\approx$1%.

C. Data acquisition and processing

The radicals are probed by the SRS beam at approximately 10 mm downstream from the throat of the expansion. The detection of the beam exiting the chamber is accomplished by an InGaAs detector equipped with its amplifier (Thorlabs). Signal digitalization is provided by a 20 MHz, 12 bit acquisition card (Measurement Computing) plugged into a personal computer running LABVIEW software.

Shot to shot ringdown time measurements are possible by using a speed-optimized algorithm capable of extracting several ringdown times from a given decay, thereby providing a means of detecting nonexponential decays. Noise is always critical to the proper fit of an exponential (or a quasiexponential) decay. The relatively high intensity of the optical signal available on the detector minimizes the photon shot noise and, hence, “technical” noise (independent of the amplitude of the signal) is dominant, at least for the significant part of the decay.

The frequency scans of the ring laser are divided in segments of $\approx$10 GHz, wherein the frequency step size can be adjusted according to the desired sampling (usually 40 MHz). A modest number (typically 4) of laser shots are averaged for each frequency point. To linearize the spectrum, a small part of the ring Ti:Sa beam is deflected to a solid Fabry-Pérot etalon (FPE) with a free spectral range of $\approx$1 GHz and simultaneously recorded. To be able to distinguish the absorption of the species produced by the discharge from other species potentially present inside the jet or the cavity, the ringdown time is recorded at each wavelength step, with the discharge on and off, and the difference is taken. Typical “parasitic” species are water or precursor molecules. However, advantage can be taken of the presence of the water molecule for calibration purposes. If the transitions used for the calibration are too weak, additional quantities of water can be injected through the mirror flushing pipes.

A typical CD$_3$O$_2$ spectrum can spread over $\approx$30 cm$^{-1}$ and includes $>1000$ discernible features. To record the entire spectrum, it has been divided into several intervals (typically 3–5 cm$^{-1}$ wide with an overlap). Each interval is linearized in 10 GHz segments by using a quadratic rectifying function determined precisely from the maxima of transmission of the FPE (zeros of the derivative). The process yields precise relative line positions. Then, the calibration of absolute frequency is obtained by using the above mentioned water lines (at least two per record) whose frequency centers are fitted and then matched with the positions provided by the HITRAN database.

III. MOLECULAR EIGENVALUES AND EIGENFUNCTIONS

The observed spectrum involves the $0^0_0^0$ band of the $\tilde{A}^2\Pi^\prime$-$\tilde{A}^2\Pi^\prime\prime$ electronic transition of methyl peroxy in the NIR. Based on chemical intuition and consistent with recent *ab initio* calculations, we expect CD$_3$O$_2$ to be an asymmetric rotor with the plane of symmetry containing the C and O atoms. While the rotor is asymmetric we expect it to be fairly near the prolate symmetric top limit since $A \gg (B-C)$. Since the radical is in a doublet state we expect an observable spin-rotation interaction as has been seen with the alkoxyl radicals that we have studied. In the room temperature spectrum, tunneling splittings have been observed for both CH$_3$O$_2$ and CD$_3$O$_2$ in excited torsional levels involving the internal rotation of the methyl group. Ergo, it is appropriate to write the total Hamiltonian as

$$\mathcal{H} = \mathcal{H}_{\text{Rot}} + \mathcal{H}_{\text{SR}} + \mathcal{H}_{\text{Tor}} + T_0(i),$$

where $T_0(i)$ is the energy of the vibronic state (vibrationless level of $\tilde{A}$ or $\tilde{X}$ electronic state) with $i=A$ or $X$ and $T_0(X)$ is taken as the zero of energy. In the following, we will neglect $\mathcal{H}_{\text{Tor}}$ as the analysis of the room temperature spectrum indicated any tunneling splitting in the vibrationless levels of CD$_3$O$_2$ of either the $\tilde{X}$ or $\tilde{A}$ state would unlikely be resolved experimentally and *ipso facto* has proven to be the case. Similarly we expect any hyperfine splittings to be well below our experimental resolution and neglect them in $\mathcal{H}$. However, the theoretical prediction is that the tunneling splitting should be resolved for CH$_3$O$_2$ and so, we explicitly include $\mathcal{H}_{\text{Tor}}$ in $\mathcal{H}$ for future reference.

Because of the expected relative weakness of the spin-rotation coupling, it is appropriate to use for $\mathcal{H}$ a case b like, symmetric top representation, $[INKSM_J]$, wherein the rotational angular momentum $N$, and the spin-angular momentum $S$ are coupled to form the resultant total angular momentum $J$. The $M_J$ denotes the projection of $J$ on the space fixed $Z$ axis and $K$ denotes the projection of $N$ on the molecular symmetry axis. Since we are neglecting $\mathcal{H}_{\text{Tor}}$ it is appropriate to write $\mathcal{H}_{\text{Rot}}$ in the principal inertial axis system where it has its usual form,

$$\mathcal{H}_{\text{Rot}} = AN_a^2 + BN_b^2 + CN_c^2.$$

The matrix elements of $\mathcal{H}_{\text{Rot}}$ are well-known. The spin-rotation Hamiltonian has been considered by many authors and can be written as...
\[ \mathcal{H}_{SR} = \mathbf{S} \cdot \mathbf{e} \cdot \mathbf{N} = \frac{1}{2} \sum_{\alpha \beta} \epsilon_{\alpha \beta} (N_{\alpha} S_{\beta} + S_{\alpha} N_{\beta}). \tag{3} \]

It is well-known\textsuperscript{35,37-41} that the second-order contribution arising from cross terms between the \textbf{L} uncoupling and the spin-orbit coupling is the predominant contributor to the tensor components \( \epsilon_{\alpha \beta} \), and it is, therefore, not surprising that they have not been determined from \textit{ab initio} calculations. Not unexpectedly, the number of nonzero spin-rotation tensorial components \( \epsilon_{\alpha \beta} \) depends on the molecule’s symmetry. For a molecule with a symmetry plane (such as methyl per-oxo), the number of nonzero components is 5. However, as has been discussed previously, these are not linearly independent for a given molecule; in other words, for a given isotopolog, only four components can be independently determined. Brown et al.\textsuperscript{42,43} suggested to eliminate the antisymmetric contribution by unitarily transforming the \( \mathbf{e} \) tensor to the reduced tensor \( \tilde{\mathbf{e}} \) (see Ref. 44 for details). We follow this example, leaving the four tensor elements, \( \tilde{\epsilon}_{\text{aa}}, \tilde{\epsilon}_{\text{bb}}, \tilde{\epsilon}_{\text{cc}}, \) and \( (\tilde{\epsilon}_{\text{ab}} + \epsilon_{\text{bc}})/2 \), to parametrize the molecule’s spin-rotation interaction. The matrix elements of \( \mathcal{H}_{SR} \) are given by Ref. 35 who adopted them from Bowater et al.\textsuperscript{45}.

Zare\textsuperscript{46} has derived a formula for the linestrength of an asymmetric top in an arbitrary spin state. Gopalakrishnan et al.\textsuperscript{35} modified it for a doublet state and Bunker and Jensen\textsuperscript{46} have derived a general formula (Eq. 14.48) for the linestrength of an asymmetric top in an arbitrary spin state. We can use and simplify that formula to obtain

\[
S(J,f',r';J',f'',r'') = g_m (2J' + 1)(2J' + 1) \left| \sum_{N''} \sum_{K'q} (-1)^{N''+N'+K'} \times [(2N''+1)(2N''+1)]^{1/2} \right. \\
\left. \times \left( \begin{array}{c} N'' \ N' \ N \ K' \\ J' \ \ J \ \ S \end{array} \right) \right| \left. \left| \langle A,0|T^f_{J}\mu|X,0 \rangle \right|^2 \right. \\
\left| \langle A,0|T^{f'}_{J'}\mu|X,0 \rangle \right|^2. \tag{4} \]

In the above, vibronic mixing is neglected and \( S \) is assumed to be a good quantum number. The nuclear spin degeneracy of the final and initial states is denoted by \( g_m \) and the mixing coefficients \( a_{N',K'}^{J,f,r} \) are assumed to be real, and \( T^f_J(\mu), q=0, \pm 1, \) is a component of the dipole moment tensor in the molecule fixed axis system. For a pure \( c \)-type transition, as is the case with the \( \tilde{A} \sim \tilde{X} \) transition of methyl per-oxo radical, the transition dipole moment lies along the \( y \) axis, which is identical to the \( c \) axis in the inertial axis system. So \( \mu_x = \mu_y = 0 \) and \( \mu_z = \mu_c \). Hence, \( \langle A,0|T^f_J(\mu)|X,0 \rangle = 0 \) and \( \langle A,0|T^{f'}_{J'}(\mu)|X,0 \rangle = (-i/\sqrt{2}) \langle A,0|\mu_c|X,0 \rangle \), where the bras and kets denote a specific vibronic state, in this case, the vibrationless level of the \( \tilde{X} \) or \( \tilde{A} \) states.

The mixing coefficients of the basis functions in the eigenfunctions have been defined in a somewhat more general and simplified manner than before\textsuperscript{35}:

\[
|Jf(\tau NK)SM_J\rangle = \sum_{N''=J-S} \sum_{K''=N''} a_{N''}^{Jf,\tau} a_{K''}^{Jf,\tau} |JN''K''S\rangle. \tag{5} \]

IV. RESULTS AND DISCUSSION

A. Spectral analysis

An overview of the experimentally observed spectrum of the \( \tilde{A} \sim \tilde{A} \), \( \tilde{X} \sim \tilde{A} \) transition of CD\textsubscript{3}O\textsubscript{2} is shown in Fig. 2. Figures 3–5 show expanded regions of Fig. 2 where the detailed structure of the spectrum is evident. These regions are assumed to be rigorously good, while \( N \) and \( K \) are not but are still useful since \( \mathcal{H}_{SR} \) is generally small compared to \( \mathcal{H}_{\text{Rot}} \) and CD\textsubscript{3}O\textsubscript{2} is fairly close to a prolate symmetric top. The “new” quantum numbers, \( f \) and \( r \), denote for a given \( J \), respectively, the spin components and the asymmetric rotor level (standardly designated by \( K_a \) and \( K_c \)).
contain, respectively, transitions identified to be of the nature, \(p_i^r Q_{ij}(J)\) and \(q_i^r Q_{ij}(J)\), \(p_i^r P_{ij}(J)\), and \(R_{ij}(J)\). The notation for individual transitions is \(\Delta N=\Delta J_i(J')\), where \(\Delta K\) and \(\Delta J = -1, 0, +1\) are represented by \(p, q,\) and \(r\) for \(\Delta K\), and \(P, Q,\) and \(R\) for \(\Delta J\), and \(i\) and \(j\) denote, respectively, the fine structure quantum numbers in the upper and lower electronic states. As expected, and later confirmed by the analysis, for a molecule with relatively weak spin-rotation coupling, transitions are mainly of the type \(\Delta N=\Delta J_i\), so \(i=j=1\) or \(2\), where \(1\) and \(2\) denote, respectively, the upper and lower spin components of a given \(N\) state for which \(N=J=1/2\). Although not rigorous, \(N\) and \(K=(K_a)\) remain as good enough quantum numbers to be useful, physically meaningful labels for the transitions.

Our subsequent analysis will indicate that the temperature of the spectra in Figs. 2–5 is 15–20 K. Nonetheless, examination of the spectrum of Fig. 2 reveals over 1000 identifiable features. In addition, there is a broad background absorption of \(\approx 0.2\) ppm/pass. This background vanishes when the optical cavity is pumped out and it can be compared to the 1\(\sigma\) noise level of \(\approx 0.04\) ppm/pass.

Even with spectra of the quality of those in Figs. 2–5, initial assignments can be very difficult considering the fact that the Hamiltonian for each of the \(\tilde{X}\) and \(\tilde{A}\) states contains three rotational constants plus four spin-rotation constants, as well as \(T_0(\tilde{A})\), for a total of 15 adjustable parameters. In addition the components of the transition dipole along the inertial axes and the rotational temperature strongly affect the appearance of the spectrum.

Fortunately, we knew in advance of the analyses quite a lot about the molecular parameters. Analysis of the room temperature spectrum yielded values of the rotational constants \((A', B', C')\), \((A'', B'', C'')\), \(T_0(\tilde{A})\). Within the precision of these values was limited, they served as excellent starting estimates.

Estimates of the spin-rotation parameters were not available from the room temperature spectrum. However, we know that the expression for the \(\tilde{E}_{\text{ab}}\) are dominated by the second-order effects of the cross terms of the \(L\) coupling and the spin-orbit coupling. These terms, in principle, couple together all the electronic states. However, the proximity in energy of the \(X^2A''\) and \(\tilde{A}^2A'\) states would indicate that the coupling between them should dominate. Since the matrix element of the \(c\) component (perpendicular to the \(C_i\) plane) of the orbital angular momentum vanishes between states of \(A''\) and \(A'\) symmetries, it is reasonable to expect all the \(\tilde{E}_{\text{ab}}\) components whose \(\alpha\) or \(\beta=\epsilon\) would be very small. We, therefore, neglect such terms except for \(\tilde{E}_{cc}\), since it alone has nonzero diagonal elements in the basis set. This yields a set of four constants \(\tilde{E}_{aa}, \tilde{E}_{bb}, \tilde{E}_{cc}\), and \((\tilde{E}_{ba}+\tilde{E}_{ab})/2\), and we expect \(\tilde{E}_{cc}\) to be significantly smaller than the other three. Moreover, in this two-state approximation for the \(\tilde{E}_{ab}\), we expect the values in the \(\tilde{X}\) and \(\tilde{A}\) states to be of the same magnitude but opposite in sign. Finally we can roughly estimate the relative values of the spin-rotation constants by referring to the experimentally determined values\(^41\) for ethoxy which has similar rotational constants. However, there is an unknown scale factor between ethoxy and methyl peroxy because the relative magnitude of the spin-orbit coupling is unknown. Nonetheless, we expect the scale factor to be considerably less than unity due to the fact that the \(\tilde{A}-\tilde{X}\) separation is much larger in methyl peroxy than in ethoxy.

In previous experiments with our slit jet, discharge temperatures of \(\approx 20\) K were obtained, so we take 20 K as the starting estimate. As mentioned earlier, barring vibronic mixing, only the \(c\) component of the dipole transition moment will be nonvanishing for an \(A''-A''\) electronic transition.

Employing all these considerations, simulations of the spectrum were run with our \textsc{specview} software. These simulations bore a good resemblance to the observed spectrum. However, it still required many iterations of parameter variations and simulations to “lock in” a spectral assignment. For the final fits, over 350 lines have been found to be relatively strong, resolved single transitions (or easily deconvoluted blends of two or at least three lines) and were used in a least squares fit to determine the parameters. However, the spec-
tional simulations were compared to the entirety of the observed spectrum with over 1000 identifiable features, with the additional spectral lines consisting mainly of more complicated blends of transitions.

Essentially, all the spectral features were reproduced, with Figs. 3–5 giving examples of the fidelity with which the experimental spectra were simulated. The effects of temperature variation on the spectrum is clearly shown in Fig. 6. The temperature variation of the experimental traces is controlled by changing the CD$_3$I precursor concentration and/or the backing pressure of the expansion. Higher seeding of the precursor causes an increase in radical concentration, temperature, and background absorption.

The 15 molecular parameters determined from the fit are given in Table II. As the table shows, particular precise determinations of the rotational constants and $T_0(\tilde{A})$ are obtained. Gratifyingly, while the parameters from the jet-cooled spectrum are much more precise than those from the room temperature experiments, all the presently determined parameters fall within the error limits expected from the room temperature work. Table III makes a detailed comparison of the previous experimental and calculated values for the $\tilde{X}$ and $\tilde{A}$ state rotational parameters of CD$_3$O$_2$. While the calculations give quite reasonable estimates of the rotational constants, it is clear that they need considerable improvement compared to the present results.

While not quite so precise, good values are also determined for the spin-rotation parameters. As anticipated, the values are essentially the same in magnitude but opposite in sign for the $\tilde{X}$ and $\tilde{A}$ states. The value of $\tilde{e}_{cc}$ is 0 within experimental error in the $\tilde{X}$ state and nonzero just beyond experimental error in the $\tilde{A}$ state for which the two-state approximation should be less valid.

Comparison with the spin-rotation parameters of ethoxy reveals that the expectation that the ratio of tensor components would be similar is upheld; i.e., for $\tilde{X}$ state CD$_3$O$_2$,

$$\frac{\tilde{e}_{bb}}{\tilde{e}_{aa}} = 0.13, \quad \frac{\tilde{e}_{cc}}{\tilde{e}_{aa}} = 0, \quad \frac{1}{2} \left( \frac{\tilde{e}_{ab} + \tilde{e}_{ba}}{\tilde{e}_{aa}} \right) = -0.19,$$

while for $\tilde{X}$ state C$_2$H$_5$O,

$$\frac{\tilde{e}_{bb}}{\tilde{e}_{aa}} = 0.11, \quad \frac{\tilde{e}_{cc}}{\tilde{e}_{aa}} = 0, \quad \frac{1}{2} \left( \frac{\tilde{e}_{ab} + \tilde{e}_{ba}}{\tilde{e}_{aa}} \right) = -0.28.$$ 

As expected, the spin-rotation tensor is significantly smaller for CD$_3$O$_2$. For example, $(\tilde{e}_{aa})_{CD_3O_2}/(\tilde{e}_{aa})_{C_2H_5O}=0.23$. Nonetheless, if anything, one might have expected a greater reduction in the ratio since the $\tilde{A}-\tilde{X}$ separation in methyl peroxo is about 20 times greater than it is in ethoxy.

Finally, a word about parameter error estimates is in order. Even with our present high resolution, it is clear from Figs. 3–6 that the spectrum is not fully resolved. Estimating the uncertainties in the fit parameters resulting from the congested spectrum is nontrivial. One approach is to compare the spectral changes resulting from varying the value of each fit parameter. One can then set uncertainties by noting the variation of the parameter required to produce a noticeable deviation between the corresponding simulated spectrum and the experimental one. This was done manually and the resulting error estimates are given in Table II. Generally speaking these estimates are approximately three times the $3\sigma$ error estimates generated from this least squares program fit. Therefore, they should be quite conservative estimates. A final note concerns the error in $T_0$ whose statistical error is

![Graph showing temperature dependence of the region of the spectrum.](image)

FIG. 6. (Color online) Temperature dependence of the region of the spectrum shown in Fig. 3. The temperature is increased by increasing the CD$_3$I seeding. The experimental data are shown in the upper traces (black, offset by 3 ppm) and the simulation in the lower traces (red).

### Table II. Fitted molecular parameters. All values are in cm$^{-1}$. The standard deviation of the difference between the energy of the calculated and observed lines is 0.0018 cm$^{-1}$. See text for a discussion of the parameter error estimates.

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{A}$</th>
<th>$\tilde{X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>7373.2739 (15)</td>
<td>0</td>
</tr>
<tr>
<td>$A$</td>
<td>1.1781 (10)</td>
<td>1.2932 (10)</td>
</tr>
<tr>
<td>$B$</td>
<td>0.327 07 (11)</td>
<td>0.320 79 (11)</td>
</tr>
<tr>
<td>$C$</td>
<td>0.283 87 (11)</td>
<td>0.285 46 (11)</td>
</tr>
<tr>
<td>$\tilde{e}_{aa}$</td>
<td>0.0695 (15)</td>
<td>-0.0718 (15)</td>
</tr>
<tr>
<td>$\tilde{e}_{bb}$</td>
<td>0.0107 (14)</td>
<td>-0.0091 (14)</td>
</tr>
<tr>
<td>$\tilde{e}_{cc}$</td>
<td>-0.0029 (15)</td>
<td>-0.0003 (15)</td>
</tr>
<tr>
<td>$\tilde{e}_{ab}$</td>
<td>0.0218 (22)</td>
<td>0.0138 (22)</td>
</tr>
<tr>
<td>$\tilde{e}_{bc}$</td>
<td>0.0283 07 (11)</td>
<td>0.0304 (11)</td>
</tr>
<tr>
<td>$\tilde{e}_{ca}$</td>
<td>0.0346 (11)</td>
<td>0.0304 (11)</td>
</tr>
</tbody>
</table>

### Table III. Rotational parameters of CD$_3$O$_2$ from various experiments and calculations.

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Expt.$^a$</th>
<th>Calc. 1$^b$</th>
<th>Calc. 2$^b$</th>
<th>Calc. 3$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A''$</td>
<td>1.2932</td>
<td>1.296</td>
<td>1.338</td>
<td>1.316</td>
<td>1.315</td>
</tr>
<tr>
<td>$B''$</td>
<td>0.320 79</td>
<td>0.332</td>
<td>0.328</td>
<td>0.304</td>
<td>0.318</td>
</tr>
<tr>
<td>$C''$</td>
<td>0.285 46</td>
<td>0.290</td>
<td>0.293</td>
<td>0.281</td>
<td>0.284</td>
</tr>
<tr>
<td>$A'$</td>
<td>1.1781</td>
<td>1.182</td>
<td>1.249</td>
<td>1.213</td>
<td>1.220</td>
</tr>
<tr>
<td>$B'$</td>
<td>0.327 07</td>
<td>0.340</td>
<td>0.331</td>
<td>0.316</td>
<td>0.320</td>
</tr>
<tr>
<td>$C'$</td>
<td>0.283 87</td>
<td>0.288</td>
<td>0.291</td>
<td>0.278</td>
<td>0.281</td>
</tr>
</tbody>
</table>

B. Line intensities

In the previous section, the information on the molecular parameters was derived exclusively from the measured frequencies of the spectral lines. As Figs. 3–6 show, the quality of the simulations in terms of relative line intensities is also very good. However, no quantitative information has been derived in Sec. IV A from the line intensities. Since CRDS is a quantitative absorption technique, additional quantitative information, e.g., radical concentration, transition dipole moments, etc., is potentially available from the intensities in the spectrum.

Experimentally, the CRDS experiment measures at the given frequency $\nu$ the ringdown time $\tau(\nu)$ with a sample and $\tau_0$ without a sample. This measurement is easily related to the single pass absorbance (which we report in ppm/pass) $A(\nu)$ in the optical cavity due to the sample,

$$A(\nu) = \alpha(\nu) \ell = \frac{L}{c} [\tau^{-1}(\nu) - \tau_0^{-1}], \quad (6)$$

where the equation is valid in the limit of small absorption which is certainly appropriate in our experiments. In the above, the parameters have the following meaning: $\alpha(\nu)$ is the absorption coefficient, $\ell$ the sample length (5 cm in our apparatus), and $L$ the optical path length (67 cm in our apparatus).

The absorption coefficient for a given transition can be related to the absorption cross section $\sigma(\nu)$ and the (total) concentration $N$ (radicals/cm$^3$) by

$$\alpha(\nu) = \frac{\sigma(\nu) N (2J' + 1)}{Q(T)} e^{-E_{2J',\nu}/kT} (1 - e^{-h\nu/kT}). \quad (7)$$

The part of Eq. (7) in square brackets gives essentially the fraction of molecules that contribute to the given transition assuming the sample is in thermal equilibrium. $E_{2J',\nu}$ is the energy of the lower level in the transition and $Q(T)$ is the partition function with $T$ the temperature in kelvin. For our experiments in the NIR, $(e^{-h\nu/kT})$ can be neglected.

The cross section can be related to the transition dipole for the vibrionic transition $0^0_0\rightarrow A^0_1-X^2\Sigma^+\rightarrow A^0_1$ through the linestrength, $S(J'f'\tau'\rightarrow J''f''\tau'')$ defined in Eq. (4), via

$$\sigma(\nu) = \frac{2\pi^2 \nu_0(J'f'\tau'\rightarrow J''f''\tau'')S(J'f'\tau'\rightarrow J''f''\tau'')}{3\epsilon_0 hc(2J' + 1)} \times g(\nu - \nu_0(J'f'\tau'\rightarrow J''f''\tau'')) \quad (8)$$

where $g(\nu - \nu_0(J'f'\tau'\rightarrow J''f''\tau''))$ is the normalized lineshape for an individual transition, centered at $\nu_0$. We can integrate $\alpha(\nu)$ over an individual transition or over the vibrionic band to get an integrated absorbance and cross section. We can define the integrated absorbance over the vibrionic band per unit length as $A_B^I$,

$$A_B^I = \int \alpha(\nu) d\nu = \sigma_B(T) N \ell. \quad (9)$$

Using Eqs. (7) and (8), the corresponding integrated cross section $\sigma_B(T)$ is given by

$$\sigma_B(T) = \frac{2\pi^2}{3\epsilon_0 hc Q(T)} \sum_\nu \nu_0(J'f'\tau'\rightarrow J''f''\tau') \times S(J'f'\tau'\rightarrow J''f''\tau') e^{-E_{2J',\nu}/kT} \quad (10)$$

In obtaining Eq. (10), we have summed over all transitions in the band and the integral over $\nu$ eliminates the normalized lineshape function.

While Eq. (9) establishes a useful relationship for the band absorbance, we note that it depends upon the product of the concentration $N$ and the unknown vibrionic transition moment component in $S(J'f'\tau'\rightarrow J''f''\tau')$. As there is no observed intensity in the spectrum from the $\mu_\alpha$ and $\mu_\beta$ components, we take them to be zero as expected for an $A^1 \rightarrow A^1$ transition. Thus, the sum of the dipole component matrix elements over $q$ reduces to the single term containing $\langle A, 0|\mu| X, 0 \rangle$.

Equation (9) has the advantage that it is a very general result, which should describe the spectrum of methyl peroxy under a variety of conditions. In particular, we can write

$$N = N_{\text{ref}} \left[ \frac{A_B^I}{A_B^I(\text{ref})} \right] \left[ \frac{\sigma_B(T_{\text{ref}})}{\sigma_B(T)} \right] \left[ \frac{\ell_{\text{ref}}}{\ell} \right], \quad (11)$$

where the quantities denoted as ref indicate a reference absorption experiment on the same species. For the reference we chose the room temperature CRDS spectrum of methyl peroxy reported in Ref. 13. From that work in which $N_{\text{ref}}$ is reported to be $1.4(2) \times 10^{15}$ radicals/cm$^3$, $A_B^I(\text{ref})$ can be obtained by numerical integration over the band as $=10(2) \times 10^{-3}$ cm$^{-1}$, after subtracting a 50 ppm/pass background. In the reference experiment, $N_{\text{ref}}$ was obtained from the rate of decay of the methyl peroxy signal and the known rate constant $[k=4.9(20) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$] for its bimolecular decay. The measured value of $(\ell_{\text{ref}}/\ell)$ = $(16 \text{ cm}/5 \text{ cm})$ = $3.2$, and the ratio of $[\sigma_B(300)/\sigma_B(15)]$ is calculated to be 0.9992 by our SPECVIEW software. For the jet-cooled spectrum we find again, by numerical integration over the band, $A_B^I(\text{air})=10(2) \times 10^{-3}$ cm$^{-1}$ after subtracting a background of 0.17 ppm/pass. Putting these values into Eq. (11) yields $N=4.5(24) \times 10^{12}$ radicals/cm$^3$ at the point of detection.

This density is comparable to the value we reported for the OH radical with a similar slit equipped with a longitudinal discharge. With that discharge we also reported a density number of CH$_3$ as $N_{\text{CH}_3}=1.2 \times 10^{13}$ radicals/cm$^3$ (results obtained on the CH stretch fundamental). We have not been able to simultaneously measure the methyl and methyl peroxy radical concentrations present in the jet, but we do not believe that the concentrations differ markedly from the above results. These numbers demonstrate a good yield for the production of methyl peroxy from methyl, in the 35%–40% range, although the majority of the methyl radicals are likely being converted to CH$_3$O. By using the usual jet...
modeling, an estimate of the peroxy radical density can be given at the throat of our slit jet as \( N_{\text{throat}} = 5.6 \times 10^{13} \text{ radicals/cm}^3 \).

Once a radical density \( N \) is known, Eq. (9) can be used to determine the cross section \( \sigma_B(T) \). Using the SPECVIEW calculation of \( \sigma_B(T) \) as a function of \( \langle A, 0 | \mu_c | X, 0 \rangle \) and Eqs. (4) and (10) yield a value for the vibronic transition moment \( \langle A, 0 | \mu_c | X, 0 \rangle \) of \( 1.2(6) \times 10^{-2} \text{ D} \). To our knowledge, this is the first experimental determination of the \( \tilde{A} - \tilde{X} \) transition moment for any peroxy radical. However, our present result is pleasingly close to the calculated value\(^{51}\) of \( 1.7 \times 10^{-2} \text{ D} \) for HO\(_2\). Unfortunately the present precision of the experimental determination of \( \langle A, 0 | \mu_c | X, 0 \rangle \) is relatively poor. It is primarily limited by the determination of \( N_{\text{ref}} \) in the room temperature experiments, since with the molecular parameters in Table II, \( \sigma_B(T) \) can be accurately calculated as a function of the dipole moment. Hopefully, future experiments will yield a more precise value of \( N_{\text{ref}} \) and, hence, \( \langle A, 0 | \mu_c | X, 0 \rangle \).

C. Lineshapes and linewidths

To provide the spectral simulations in Figs. 3–6, a lineshape and linewidth must be assumed for the individual transitions. The SPECVIEW software allows a simulation of the lines with a Lorentzian, Gaussian, or Voigt profile. From a past work\(^{24}\) we can estimate an “instrumental linewidth” in the NIR of \( \approx 250 \text{ MHz} \), as a combined result of residual Doppler broadening in the slit jet and the bandwidth of our SRS source. Both of these contributions should be Gaussian in nature, and we have confirmed that the observed lines of jet-cooled H\(_2\)O and CH\(_3\)I in our apparatus are well fitted by a Gaussian linewidth of \( \approx 250 \text{ MHz} \).

However, it is obvious from the experimental traces that a broader line is generally observed for the CD\(_3\)O\(_2\) transition. This is shown in more detail in Fig. 7 where a “typical” portion of the spectrum is enlarged and compared with the predicted spectrum represented by a stick plot and also with simulations employing lines of various shapes and widths. It is clear from Fig. 7 that to match the resolution between peaks in the spectrum, a Gaussian of linewidth (FWHM) of nearly 500 MHz would be required. However, such a simulation still does a poor job of simulating the region between lines. After some trial and error we see from Fig. 7 that a Voigt profile with equal widths of 300 MHz for the Gaussian and Lorentzian components reproduces rather well the experimental trace. Checking other regions of the spectrum confirms that the 300/300 Voigt profile overall does a good job of reproducing the experiment. Given the overlap in the spectrum and the correlation between the Gaussian and Lorentzian components, it means that the width determination is not particularly precise. Nonetheless, it appears rather certain that the spectrum requires a Voigt profile with comparable Lorentzian and Gaussian widths of around 300 MHz.

The Gaussian component is relatively easy to understand. As mentioned we expect an instrumental Gaussian linewidth of \( \approx 250 \text{ MHz} \). We also expect torsional tunneling splittings in the range of 100–200 MHz. A pair of 250 MHz Gaussians separated by \( \approx 150 \text{ MHz} \) is well represented by a 300 MHz Gaussian.

The Lorentzian component is harder to explain. It presumably arises from lifetime (\( \approx 1 \text{ ns} \) broadening, most likely present in the excited \( \tilde{A} \) state. The fact that a dynamical process is occurring this fast in the vibrationless level of the \( \tilde{A} \) state at only 7373 cm\(^{-1} \) of excitation is somewhat surprising. Interestingly, there is evidence that there is an even greater broadening, corresponding to a somewhat shorter lifetime, involved in the spectrum of CH\(_3\)O\(_2\). We, therefore, defer further discussion of this matter until we complete the analysis of the CH\(_3\)O\(_2\) spectrum.

V. CONCLUSIONS

The nearly rotationally resolved spectrum of the \( 0^0_0 \) band of the \( \tilde{A}^2\tilde{A}'-\tilde{X}^2\tilde{A}'' \) electronic transition of the perdeutero methyl peroxy radical has been observed in the NIR using the CRDS technique. The observation is made possible by the use of a narrow band radiation source and cooling of the radical in a supersonic slit-jet discharge down to 15 K. Over 1000 features in the rovibronic spectrum can be discerned and least squares fits have been performed using over 350 unblended, or nearly unblended, lines. These fits have led to a set of 15 precisely determined molecular parameters describing the \( \tilde{X} \) and \( \tilde{A} \) states. These include for each state, three rotational constants and four spin-rotation parameters as well as the energy separation of the vibrationless level of the two states. This set of parameters faithfully simulates not only the \( \approx 350 \) lines used in the fits but also essentially all of the \( >1000 \) observed spectral features. These parameters, particularly the spin-rotation tensor components, have been compared to those reported for comparable alkoxo radicals and to expectations based upon the electronic structure of methyl peroxy.

Tunneling splittings have been observed for more highly excited methyl torsional levels in the room temperature spectra of both CH\(_3\)O\(_2\) and CD\(_3\)O\(_2\). No direct evidence for tunneling splittings in the present spectrum involving the \( 0^0_0 \) band of CD\(_3\)O\(_2\) has been observed and an upper limit of...
≈200 MHz can be placed on these splittings. This value is consistent with both theoretical calculations and the empirical determination from the room temperature spectrum of a barrier of ≈325 cm⁻¹ in the X state and much higher in the A state. Such a barrier would be required to give rise to a tunneling splitting of 100–200 MHz in the vibrationless level of the X state.

The above mentioned simulation not only well reproduces the frequencies of the spectra lines but also their relative intensities. Combining this with the absolute absorbance measurements offered by CRDS provides the opportunity to estimate, using the room temperature spectra as a reference, the concentration of CD₃O₂ at the observation point in the jet to be 4×10⁻³ cm⁻³. The use of this density, in turn, allows a determination of the vibronic transition moment (A₁,0|μ|X₁,0)=0.012 D. The precision of these two measurements is not high. Nonetheless, they demonstrate the potential to measure absolute concentrations and transition moments, notoriously difficult to obtain but extremely important quantities for transient, reactive species.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of this work by the National Science Foundation via Grant No. CHE-0511809. They also wish to thank Dr. Vadim Stakhursky for providing help on the SPECVIEW code. P.D. wishes to thank Dr. Trevor Sears for fruitful conversations about spin-rotation coupling.

17 S. J. Zalyubovsky, B. G. Glover, T. A. Miller, C. Hayes, J. K. Merle, and