Vibronic spectroscopy of the peroxyacetyl radical in the near IR

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**Vibronic spectroscopy of the peroxyacetyl radical in the near IR**

Y. J. Hu, H. B. Fu, and E. R. Bernstein

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The $\tilde{\text{A}}^2\text{A}' \rightarrow \tilde{\text{X}}^2\text{A}''$ electronic transition of the peroxyacetyl radical (PA) is observed employing NIR/VUV ion enhancement, supersonic jet spectroscopy. Rotational envelope simulations yield a rotational temperature for ground state PA of ca. 55 K. *Ab initio* calculations of transition energies and vibrational frequencies for the $\tilde{\text{A}} \rightarrow \tilde{\text{X}}$ transition assist in the assignment of the observed spectrum. A number of the vibrational modes of the $\tilde{\text{A}}$ state are assigned to observed transitions (the O–O stretch $2^1$, the COO bend $5^1$, and the CCOO backbone bend $6^1$). The calculations and mass spectra suggest that the ground state of the PA ion is repulsive. An increase in rotational linewidth of the overtone of the O–O stretch ($2^1$) is observed and discussed in terms of $\tilde{\text{A}}$ state dynamics. The O–O stretch anharmonicity is estimated to be 13.35 cm$^{-1}$. © 2006 American Institute of Physics.

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**I. INTRODUCTION**

Organic peroxy radicals are suggested to be involved in a number of atmospheric processes: the production of photochemical smog, the formation and precipitation of acids, and the emission of trace species, such as carbon monoxide and volatile organic compounds. The peroxyacetyl radical [PA, CH$_3$C(O)OO] is one of the most important atmospheric peroxy radicals, and it can react with NO$_2$ to form peroxyacetyl nitrate [PAN, CH$_3$(C(O)OO)NO$_2$], an additional important atmospheric species that can serve as a temporary reservoir and transport molecule for NO$_x$.

The vast majority of direct studies of PA employs the detection of its UV $\tilde{\text{B}}^2\text{A}'' \rightarrow \tilde{\text{X}}^2\text{A}''$ electronic transition; however, despite its large absorption cross section ($\sim$10$^{-18}$ cm$^2$), this transition is to a dissociative state, yielding little or no structure information concerning PA. The low lying electronic transition to the $\tilde{\text{A}}$ state, $\tilde{\text{A}}^2\text{A}' \rightarrow \tilde{\text{X}}^2\text{A}''$ (ca. 6000 cm$^{-1}$), is thus the only candidate for generation of vibronic spectra of PA that can yield structural and bonding information. The $\tilde{\text{A}} \rightarrow \tilde{\text{X}}$ transition of organic peroxy radicals has been observed for several species employing absorption and intracavity laser studies. Recently, cavity ringdown absorption studies have been reported for peroxy radicals in this region, and sharp, structured, well-resolved spectra (at 300 K) have been detected for PA.

In this work flash pyrolysis, supersonic expansion, and infrared/ultraviolet ion enhancement spectroscopy techniques are employed to detect and study the PA radical $\tilde{\text{A}}^2\text{A}' \rightarrow \tilde{\text{X}}^2\text{A}''$ transition. A well-resolved vibronic spectrum of PA is obtained and *ab initio* calculations are performed to enable its assignment.

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**II. EXPERIMENTAL PROCEDURES**

**A. Generation of the peroxyacetyl radical**

PA is generated from PAN by flash pyrolysis. PAN is prepared by the acid catalyzed nitration of peracetic acid [CH$_3$C(O)OOH] in tridecane solvent. Synthesis of PAN is performed according to the method of Nielson et al. and Gaffney et al., as modified by Williams et al. The synthesis and handing of PAN is described in a previous publication from this laboratory. PA can be generated from PAN by two techniques: photolysis and pyrolysis. These two methods are typically interchangeable, generating the same radical in most, but not all instances. Our laboratory has employed both of these approaches previously to generate methoxy, benzyls, cyclopentadienyls, NCO, picolys, and other radicals.

Numerous experimental studies have shown that the thermal decomposition of PAN occurs only via a NO$_2$ producing channel (nitrile O–N bond cleavage),

$$\text{CH}_3\text{C(O)O}_2\text{NO}_2(\text{PAN}) \rightarrow \text{CH}_3\text{COOO} \cdot + \text{NO}_2,$$

with no contribution from a NO$_3$ producing channel (peroxy O–O bond cleavage),

$$\text{CH}_3\text{C(O)O}_2\text{NO}_2(\text{PAN}) \rightarrow \text{CH}_3\text{COO} \cdot + \text{NO}_3,$$

even though the channels are predicted to be nearly isoenergetic. It has been argued that the thermal decomposition via (1) is favored over (2) because (1) dissociation proceeds without a barrier. Thus pyrolysis appears to be the method of choice for the generation of PA from PAN. The basic flash pyrolysis/supersonic pulsed nozzle design was first reported by Kohn et al. Our own version of this design is described in detail previously. Briefly, a 4.5 mm o.d. and a 0.8 mm i.d. alumina tube (Versus McDonald Co.) with a length of 1 in. is attached to a General Valve Series 9 pulsed solenoid valve. Both the alumina tube and the nozzle are coaxial. Heater wire (Ari Co.) is wound around the Al$_2$O$_3$ extension tube and coated with alumina cement (Cotronics...
B. NIR/VUV detection of the peroxyacetyl radicals

Employing vacuum ultraviolet (VUV) and near IR light sources, the $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$ electronic transition of PA radicals can be detected. The ionization energy (IE) of PA is about 11 eV,\textsuperscript{16} thus, the radicals can be ionized by employing one VUV photon (118 nm) and one near IR photon (1.54 μm). While the wavelength of VUV light is fixed, the IR/NIR laser is scanned to excite the jet-cooled radicals to their first electronic excited state ($\tilde{A}$ state). The VUV absorption of PA will be different for the ground state and the excited state (mostly the latter absorption will be increased), and ion signal intensity will be enhanced following the radical excitation. Thus, IR absorption spectra of the radicals can be recorded by using the mass resolved excitation spectroscopy (MRES) technique. VUV (118 nm) light is generated from the third harmonic of the Nd:YAG (yttrium aluminum garnet) laser (~25 mJ/pulse, maximum energy), tripled in a Xe/Ar mixture at 1:10 relative concentration for 200–500 Torr of total pressure.\textsuperscript{12,17} Tunable IR radiation in this wavelength range (1–2 μm) can be conveniently generated with an optical parametric oscillation (OPO) pumped by 532 nm laser radiation, generated by doubling the fundamental output of a seeded Nd/YAG laser. The VUV photons (~5 μJ/pulse or ~5 x 10\textsuperscript{12} photons/pulse) are focused into the vacuum chamber to ionize the radicals by single photon ionization. The nominal bandwidth of the OPO laser system output is 3 cm\textsuperscript{-1}. Employing an injection seeded Nd/YAG pump source and a grating tuning mirror assembly in place of the rear OPO optic reduces the IR output bandwidth further to ca. 0.4 cm\textsuperscript{-1}. The output power of this laser system is ~4 mJ/pulse from 1.0 to 2.1 μm. The whole time-of-flight mass spectroscopy (TOFMS)/MRES technique has been described in detail previously.\textsuperscript{12}

C. Computational methods

To analyze and predict the observed spectra, and in general to support the study of new species, ab initio calculations are performed on PA using the GAUSSIAN 98 package.\textsuperscript{18} All geometries of the species are fully optimized at the second-order Möller-Plesset perturbation (MP2) level with an aug-cc-pVDZ basis set. Energies are computed by performing single point calculations at the MP4(SDTQ)/aug-cc-pVDZ level of the theory from the geometries calculated at the MP2/aug-cc-pVDZ theory level. The first excited state of the PA is predicted by the single excitation configuration interaction (CIS)/6-31G(d) calculation method. Higher level calculations for geometry optimization and single point energy calculation for the excited state are also performed. Two conformers of PA exist, trans and cis. These two conformers can interconvert by O–O internal rotation around the C–O bond; the energy of the trans form is lower by ca. 300 cm\textsuperscript{-1} than the cis form.\textsuperscript{8} The trans PA conformer is thought to be the only one populated in the supersonic jet experiment. Harmonic frequency calculations for the trans PA conformer at the MP2/aug-cc-pVDZ level of theory are also performed for both $\tilde{X}$ and $\tilde{A}$ states.

III. RESULTS AND DISCUSSION

A. Calculations

The structures of cis and trans PA in the $\tilde{X}^2A''$ state, the $\tilde{A}^2A'$ states, and the ground state of the ion are shown in Fig. 1. The optimized geometries indicate that the electronic excitation $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$ mainly induces the following changes in geometry: $\Delta R_{C1-O7} = -0.045$ Å, $\Delta R_{C7-O8} = 0.067$ Å for
trans PA; and \( \Delta R_{C1-O7} = -0.064 \, \text{Å}, \Delta R_{C7-O8} = 0.066 \, \text{Å} \) for cis PA. The results suggest that the terminal O–O bond is most changed in the vibronic transition \( \bar{A} \rightarrow \bar{X} \) for cis PA; however, vibrational frequency calculations for the \( \bar{A} \rightarrow \bar{X} \) state of cis PA at the MP2/aug-cc-pVDZ level of theory yield one imaginary frequency. This suggests that cis PA on the excited \( \tilde{A} \) state is a first-order saddle point and thus not a stable structure. Based on these calculations, the PA ion ground state surface has its terminal O–O moiety far from the rest of the radical and the separation of these two oxygen atoms decreases. Based on these calculations, the PA ion ground state is obviously a repulsive state and will generate the CH\(_3\)CO\(^+\) radical ion and O\(_2\) molecule.

Given these geometry results for the optimized structures of the \( \bar{X} \) and \( \tilde{A} \) states of PA, the vibrational modes 2 (O–O stretch), 5 (COO bend), and 6 (CCOO backbone bend) should have significant intensity in the \( \tilde{A} ← \bar{X} \) vibronic structure.

Table I summarizes the results of the single point energy calculations for PA. The calculated transition energy for the trans PA conformer is predicted to be ca. 5659 cm\(^{-1}\), which is close to the observed value of 5582.5 cm\(^{-1}\). Thus, the predicted energies calculated at the MP4(SDTQ)/aug-cc-pVDZ level of theory using geometries calculated at the MP2/aug-cc-pVDZ level of theory are believable. The adiabatic IEs for both trans and cis PA are predicted as 9.1 and 9.2 eV, respectively. The calculated vertical IEs, which are the important quantities related to photoionization, are 10.8 eV for trans and 11.7 eV for cis PA, respectively. The electronic excitation energy \( (T_e) \) for trans PA is predicted to be higher by ca. 1000 cm\(^{-1}\) than the \( \tilde{A} ← \bar{X} \) origin transition \( (T_{00}) \) (see Table II).

### B. Experiments

#### 1. Observation of the spectra

The species generated by thermal decomposition of PAN and expanded in the vacuum system through the supersonic nozzle are photoionized by VUV (118 nm) light and detected

### Table I. Energies of PA based on \textit{ab initio} calculations at MP4(SDTQ)/aug-cc-pVDZ level of theory using the geometry calculated at the MP2/aug-cc-pVDZ level of theory.

<table>
<thead>
<tr>
<th>Isomers</th>
<th>Vertical IE (eV)</th>
<th>Adiabatic IE (eV)</th>
<th>( T_e ) (cm(^{-1}))</th>
<th>( T_{00} ) (cm(^{-1}))</th>
<th>( \Delta E_{trans-cis} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans</td>
<td>10.8</td>
<td>9.2</td>
<td>6690</td>
<td>5659</td>
<td>325</td>
</tr>
<tr>
<td>Cis</td>
<td>11.7</td>
<td>9.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^1 \)Difference in energies of PA between trans and cis conformers in the ground state.

### Table II. Assignment of the vibronic \( \tilde{A} \rightarrow \bar{X} \) spectrum of PA (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Peak position</th>
<th>( v_i - 0_0^i )</th>
<th>( \tilde{A} \rightarrow \bar{X} ) excited state</th>
<th>Vibration mode in ( \tilde{A} ) excited state</th>
<th>( \tilde{A} \rightarrow \bar{X} ) origin transition</th>
<th>Intensity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5582.5</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5735.5</td>
<td>153</td>
<td></td>
<td></td>
<td></td>
<td>w</td>
<td>C–H stretch(^c)</td>
</tr>
<tr>
<td></td>
<td>5756</td>
<td>173.5</td>
<td></td>
<td></td>
<td></td>
<td>w</td>
<td>C–H stretch(^c)</td>
</tr>
<tr>
<td></td>
<td>5815</td>
<td>232.5</td>
<td></td>
<td></td>
<td></td>
<td>w</td>
<td>C–H stretch(^c)</td>
</tr>
<tr>
<td></td>
<td>5852.3</td>
<td>269.8</td>
<td>269</td>
<td>7(^1) backbone</td>
<td></td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5883</td>
<td>300.5</td>
<td></td>
<td></td>
<td></td>
<td>w</td>
<td>C–H stretch(^c)</td>
</tr>
<tr>
<td></td>
<td>6055.9</td>
<td>473.4</td>
<td>443</td>
<td>6(^1) CCOO backbone</td>
<td></td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6120.6</td>
<td>538.1</td>
<td>510</td>
<td>5(^1) COO bend</td>
<td></td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6208.1</td>
<td>625.6</td>
<td>Hot band</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>6342.4</td>
<td>759.9</td>
<td>729</td>
<td>4(^1) backbone</td>
<td></td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6424</td>
<td>841.5</td>
<td>932</td>
<td>3(^1) backbone</td>
<td></td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6510.9</td>
<td>928.4</td>
<td>1079</td>
<td>2(^1) O–O stretch</td>
<td></td>
<td>s</td>
<td>Vertical excitation</td>
</tr>
<tr>
<td></td>
<td>6593.6</td>
<td>1011.1</td>
<td>5(^1) 6(^1)</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>6631</td>
<td>1048.5</td>
<td>5(^2)</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>6660.2</td>
<td>1077.7</td>
<td>Hot band</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>6726.3</td>
<td>1143.8</td>
<td>1104</td>
<td>1(^1) backbone</td>
<td></td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6777.4</td>
<td>1194.9</td>
<td>2(^1) 7(^1)</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>6806</td>
<td>1223.5</td>
<td>4(^1) 5(^1)</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>6978.2</td>
<td>1395.7</td>
<td>2(^1) 6(^1)</td>
<td></td>
<td></td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7015.1</td>
<td>1432.6</td>
<td>3(^1) 5(^1)</td>
<td></td>
<td></td>
<td>w</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td>7041</td>
<td>1458.5</td>
<td>2(^1) 4(^1)</td>
<td></td>
<td></td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7412.7</td>
<td>1830.1</td>
<td></td>
<td>2(^2)</td>
<td></td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7954.4</td>
<td>2371.9</td>
<td>2(^2) 5(^1)</td>
<td></td>
<td></td>
<td>w</td>
<td></td>
</tr>
</tbody>
</table>

\( ^c\)Calculated at MP2(FCC)/aug-cc-pVDZ level of theory, scaled by 0.937.

\( ^d\)Intensity: s: strong, m: medium, and w: weak.

\( ^e\)C–H stretch first overtone in the ground state.
by time of flight mass spectrometry. Three main features are present in this mass spectrum at $m/z$ values of 42, 43, and 46 (see Fig. 2): they are assigned as CH$_3$CO$^+$, CH$_2$CO$^+$, and NO$_2^+$, respectively. With the nozzle at room temperature, these three features are very weak and probably arise from the photodissociation of PAN by VUV light. When the tube attached to the nozzle is heated, intensities of the three peaks increase simultaneously. The species CH$_3$CO (ketene) arises from the thermal decomposition of PA.\textsuperscript{14} Thermal decomposition mechanisms for PA are discussed in a previous report from this laboratory.\textsuperscript{15} Both IEs of CH$_2$CO and NO$_2$ are below 10 eV [9.64 eV (Ref. 19) for CH$_2$CO and 9.60 eV (Ref. 20) for NO$_2$] and both can be ionized by a single photon of VUV light. Photochemical processes are different for PA, however. \textit{Ab initio} calculations predict that the vertical IE of the \textit{trans} PA is 10.8 eV (the absolute maximum error is ca. 0.4 eV),\textsuperscript{21} which is consistent with the reported data.\textsuperscript{16} Thus, a single VUV (118 nm) photon is possibly sufficient for the ionization of PA, although this energy is just at threshold. Optimized geometries of PA in the ground state, the first excited state, and the ground state of the ion (Fig. 1) suggest that the PA in the ground state and first excited state have similar geometries; however, the PA ion ground state is repulsive, implying that the PA parent ion will not be observed. The mass spectra support the above analysis. The broad peak corresponding to CH$_3$CO$^+$ can only be observed when the pyrolysis nozzle is heated. Compared to the TOFMS features for CH$_2$CO and NO$_2$, the peak FWHW for CH$_3$CO is broad (10 vs 45 ns). This suggests that PA is fragmented following the ionization by a single VUV (118 nm) photon. With the temperature of the pyrolysis nozzle kept at 330 °C, tuning the OPO laser light to vibronic transitions increases the intensity of CH$_3$CO peak by as much as 30%, while the others remain constant.

Thus we conclude that only the CH$_3$CO radical signal relates to the photodissociation (at ionization) of PA.

As discussed above, the energy of one VUV photon is just at the ionization threshold of PA and an added IR photon energy to a PA should increase the ionization cross section. Figure 3 shows the $\tilde{A} \, ^2A' \leftrightarrow \tilde{X} \, ^2A''$ vibronic transition spectrum of PA in the near IR, obtained by monitoring CH$_3$CO$^+$, the mass channel, and scanning the IR laser, with the 118 nm laser fixed to ionize PA. The spectrum shows a strong absorption at 5582.5 cm$^{-1}$ that corresponds to the origin transition of the $\tilde{A} \, ^2A' \leftrightarrow \tilde{X} \, ^2A''$ electronic transition of \textit{trans} PA. Our result is consistent with the report of Zalyubovsky et al.\textsuperscript{8} Simulated rotational contours of the transition (SPECVIEW software package\textsuperscript{25}) yield a rotational temperature for PA in the supersonic jet of roughly 55 K (see Fig. 4).

2. Spectrum assignment and analysis

Only the transitions to symmetric modes in the $\tilde{A}$ state are allowed from the vibrationless level of the $\tilde{X}$ state. The unpaired electron for the PA radical is localized on the terminal oxygen, and thus, modes involved with the motion of the terminal oxygen are expected to be most active for this transition. We can assign most of the individual peaks in the PA $\tilde{A} \rightarrow \tilde{X}$ spectrum based on this assumption.

Assignment of the spectrum employing \textit{ab initio} calculations for the vibrational modes of the $\tilde{A}$ state are shown in Fig. 3 and Table II. \textit{Ab initio} calculations suggest that the transition from the ground electronic state to the O–O stretching vibration (2$^1$) in the $\tilde{A}$ state will be an important vibronic feature for vertical excitation. The frequency of this vibrational mode is calculated as ca. 1080 cm$^{-1}$. In the spectrum shown in Fig. 3, a strong peak located at 6511 cm$^{-1}$ and shifted from the origin by 928.4 cm$^{-1}$ can be assigned as the O–O stretch (2$^1$) in the $\tilde{A}$ state. Similarly, another strong peak located at 7413 cm$^{-1}$, separated from the origin by ca. 1830 cm$^{-1}$, is suggested to be the overtone of this O–O stretch (2$^2$) in the $\tilde{A}$ state.

Two more features that can be identified in the spectrum are associated with the COO (5$^1$) bend and CCOO (6$^1$) backbone vibrational modes in the excited state. The former is located at ca. 6121 cm$^{-1}$, shifted from the origin by $\sim$538 cm$^{-1}$ and the latter is at ca. 6056 cm$^{-1}$, separated from the origin by 473 cm$^{-1}$. These two energies of the observed 5$^1$ and 6$^1$ modes are in good agreement with the calculations.
Further confirmation of these assignments comes from another two medium intensity peaks located at ca. 6978 and 7041 cm\(^{-1}\). These are assigned as the combination bands \(2^1\) and \(2^1\) respectively. Combination band \(2^1\) can also be assigned in the spectrum located at ca. 7954 cm\(^{-1}\). Weaker features, whose assignments became less certain, are also observed in the spectrum. With the assistance of \textit{ab initio} calculations, the peak at 5852 cm\(^{-1}\) can be assigned as due to the CCOO backbone mode \(?\). The peaks located at 6342, 6424, and 6726 cm\(^{-1}\) are assigned as the other backbone modes \(4^1, 5^1,\) and \(1^1\) respectively of PA in the \(A\) state. The other weak features of the \(A→\bar{X}\) transition are likely due to combination bands and hot bands. All possible assignments are listed in Table II. Based on \textit{ab initio} calculations for the ground state of PA, the four additional weak bands observed around 5800 cm\(^{-1}\) may be associated with \(\text{C}–\text{H}\) overtones of the ground state, as no more active vibrational modes can be assigned for the excited state around that energy.

### 3. 2\(^2\) O–O stretch overtone in the \(\bar{A}\) state

Figure 4 shows the observed and simulated rotational contours for the \(0^0, 2^1\), and \(2^2\) transitions of the \(\bar{A}→\bar{X}\) PA transition.\(^{22}\) Table III lists the rotational constants of the trans PA ground state and excited state obtained from \textit{ab initio} calculations. These values are used in the simulation analysis. For these three spectral features \((0^0, 2^1,\) and \(2^2\)), the FWHM of the bands are 7.3, 10.2, and 11.8 cm\(^{-1}\), respectively. The linewidths of the simulated rotational contours for these transitions increase from 0.45 to 0.9 cm\(^{-1}\). The IR laser linewidth is \(\sim 0.4\) cm\(^{-1}\) for all these features. Similar linewidth results for overtone fractures are reported by Wei and Reisler\(^{23}\) for the O–H stretch mode of the \(\text{CH}_2\text{OH}\) radical \(\bar{X}\) state. Three possibilities can be considered as the cause of this increased rotational linewidth: (1) homogeneous (dynamical) broadening, as observed for the OH stretch second overtone in methanol and hydroxylamine;\(^{24,25}\) (2) spectral overlap of a few sharp transitions involving mixed states that borrow oscillator strength from the O–O overtone; and (3) possible change in the upper state rotational constants at higher energy. Due to the bandwidth (\(\sim 0.4\) cm\(^{-1}\)) of the IR laser radiation and the lack of further information on PA, these three possibilities cannot be readily distinguished.

For the O–O stretching vibration of PA in the \(\bar{A}\) state, the energies for the fundamental and first overtone should follow the Birge-Sponer relation: \(\Delta v/v = A + Bv\), where \(\Delta v\) is the transition frequency in wave numbers (928.4 and 1830.1 cm\(^{-1}\)), \(v\) is the quantum number of the stretching vibration \((v=1, 2), (A−B)\) is the harmonic or mechanical energy of mode \(2^1\), and \(−B\) is the anharmonicity.\(^{24}\) The \(2^1\) O–O stretch anharmonicity for PA in the \(\bar{A}\) state can thus be estimated as 13.35 cm\(^{-1}\) in this work and \(A=941.75\) cm\(^{-1}\). (Note that \(\omega_0 = A−B = 941.75 + 13.35\) cm\(^{-1}\) = 955.1 cm\(^{-1}\) and that \(\omega_c x_c = B = 13.35\) cm\(^{-1}\)).

#### IV. CONCLUSION

The \(\bar{A}^2A^′←\bar{X}^2A^\prime\) electronic transition of the peroxyacetyl radical using NIR/VUV ion enhancement spectros-
copy is observed and analyzed. Rotational envelope simulations show that the rotational temperature for PA in the ground state is ca. 55 K.

*Ab initio* calculations are performed on the PA radicals. The transition energies and the vibrational frequencies for the $\tilde{A} \leftarrow \tilde{X}$ transition and the $\tilde{A}$ state are calculated to assist in the assignment of the spectrum. Vibronic transitions involving the O–O stretch $^{2 \infty}$, COO bend $^{5 \infty}$, and CCOO backbone $^{6 \infty}$ modes are identified. Geometry optimization calculations and mass spectra suggest that the ion ground electronic state of PA is a repulsive state. An increase in rotational linewidth of the overtone of the O–O stretch is observed and discussed. The O–O stretch anharmonicity in the $\tilde{A}$ state is estimated at 13.35 cm$^{-1}$.

**ACKNOWLEDGMENTS**

This work was supported in part by the NSF and by Philip Morris USA.

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