INVITED ARTICLE

Examining the ground and first excited states of methyl peroxy radical with high-level coupled-cluster theory

Andreas V. Copan, Henry F. Schaefer III and Jay Agarwal*

Center for Computational Quantum Chemistry, University of Georgia, Athens

(Received 15 May 2015; accepted 8 June 2015)

Peroxy radicals (RO₂) are intermediates in fuel combustion, where they engage in efficiency-limiting autoignition reactions. They also participate in atmospheric chemistry leading to the formation of unwanted tropospheric ozone. Advances in spectroscopic techniques have allowed for the possibility of employing the lowest (\(\tilde{A} \rightarrow \tilde{X}\)) electronic transition of RO₂ as a tool to selectively monitor these species, enabling accurate kinetic values to be obtained. Herein, high-level ab initio methods are employed to systematically refine spectroscopic predictions for the methyl peroxy radical (CH₃O₂), one of the most abundant peroxy radicals in the atmosphere. In particular, vibrationally corrected geometries and anharmonic vibrational frequencies for both the ground (\(\tilde{X}\tilde{A}^\prime\)) and first excited (\(\tilde{A}\tilde{A}^\prime\)) state are predicted using coupled-cluster theory with up to perturbative triples [CCSD(T)] and large atomic natural orbital basis sets. Equation-of-motion coupled-cluster theory is utilised to compute vertical \(\tilde{A}\tilde{A}^\prime \rightarrow \tilde{X}\tilde{A}^\prime\) transition properties; a radiative lifetime of 4.7 ms is suggested for the excited state. Finally, we predict the adiabatic excitation energy (\(E_a\)) via systematic extrapolation to the complete basis limit of coupled-cluster with up to full quadruples (CCSDTQ). After accounting for several approximations, and including an anharmonic zero-point vibrational energy correction, we match experiment for this transition to within 9 cm⁻¹.

Keywords: methyl peroxy radical; equation-of-motion; coupled-cluster; transition energy; anharmonic frequencies

1. Introduction

The chemistry of peroxy radicals (RO₂) appears in the combustion and consumption of hydrocarbon compounds, as well as the oxidation of volatile organic compounds in the atmosphere [1–4]. Understanding the reactivity of these radicals is necessary for modelling the vast network of reactions that ensue in either case [5]. For example, the propensity of RO₂ species to promote autoignition via isomerisation and further oxidation impacts combustion efficiency, and quantifying the kinetic rates of these reactions allows for the design of optimal fuel mixtures. In the atmosphere, the interaction of peroxy radicals with nitric oxides yields unwanted tropospheric ozone [6]—determining the kinetics of these low temperature pathways aids in the understanding of smog formation in polluted areas. In this research we examine the simplest RO₂ species, methyl peroxy radical (CH₃O₂).

Rate constants for the aforementioned processes are often determined in the laboratory using ultraviolet (UV) or infrared (IR) absorption as a tool to monitor the depletion of reactants, formation of products, and, in some cases, the generation of intermediates [7,8]. All peroxy radicals exhibit a strong absorbance in the UV region (200–300 nm), which corresponds to an \(\tilde{B} \rightarrow \tilde{X}\) excitation; studies employing this transition dominate the literature [9]. Unfortunately, this absorption is broad and lacks features specific to R, masking underlying absorbers and making the differentiation of individual RO₂ compounds difficult.

Vibronic spectroscopy in the IR, corresponding to an \(\tilde{A} \rightarrow \tilde{X}\) excitation, mitigates this dilemma and yields structured spectra [8,10,11]. Although this is a relatively weak transition, advances in spectroscopic techniques—including cavity ring-down [12–15], IR/vacuum-UV ionisation [16], and negative-ion photoelectron spectroscopies [17]—have fostered interest in this absorbance as a tool for monitoring peroxy radicals. The abundance of information available from vibronic IR spectra even allows for the identification of individual conformers provided that the transitions are known a priori. Prior experimental investigations of the ground-state vibrational transitions—either in the gas phase [11,17,18] or within an inert matrix [19,20]—have aided in these assignments. Theoretical work has also helped to disentangle the complex spectra of the ground and first excited states [8,21–33], but relatively few high-level ab initio studies are available; many have been limited to HO₂ [3,19,34–39].

For CH₃O₂, the lowest excited states correlate adiabatically with ground-state CH₃ (\(\tilde{X}\tilde{X}^2\Sigma^+\)) and the lowest three states of O₂ (\(\tilde{X}\tilde{X}^3\Sigma^–, \tilde{A}\tilde{A}^1\Delta, \tilde{B}\tilde{B}^1\Sigma^+\)), which gives rise to the five states shown in Figure 1. The ground
Figure 1. Correlation diagram showing the low-lying states of the methyl peroxy radical, which arise adiabatically from the association of ground-state methyl radical with molecular oxygen in its three lowest electronic states. Next to the term symbols for CH₃ and O₂, their Cₓ projections are given in parentheses.

The adiabatic electronic state (\(\tilde{X}^2A''\)) has an electron configuration of \((1a')^2...\) and correlates with the \(\tilde{X}^\prime\Sigma_g^+\) state of O₂ at the C–O dissociation limit. The first (\(\tilde{A}^2A'\)) and second (\(\tilde{B}^2A''\)) excited states arise from the two components of the \(\tilde{a}^1\Delta_g\) state on O₂ at the dissociation limit. These two states correspond to \(10a' \rightarrow 3a''\, (n \rightarrow \pi^*)\) and \(2a'' \rightarrow 3a''\, (\pi \rightarrow \pi^*)\) transitions from the ground state, respectively. Early theoretical work on the excited states of CH₃O₂ [27] found that it shares many of these general features with the simplest peroxy radical, HO₂ [29,32], including the ordering of states and the structure of the R–O vibrational frequencies computed for both the ground (\(\tilde{X}^2A''\)) and first excited (\(\tilde{A}^2A'\)) states using CC methods with perturbative triples or higher. The full NASA Ames atomic natural orbital (ANO) basis set \([H:4s3p2d1f], \, Li-Ne:[4s4p3d2f1g]; \, termed ANO2) or the truncated ANO1 basis set \([H:4s2p1d], \, Li-Ne:[4s3p2d1f]) [47]. ANO2 and ANO1 are of roughly quadruple-ζ and triple-ζ quality, respectively.

Herein, we employ coupled-cluster (CC) methods to study several key spectroscopic features of methyl peroxy radical. An earlier study of ours probed the ground-state spectroscopy of this species [34], and we now report spectroscopic parameters for the first excited state. Vibrationally corrected equilibrium geometries, adiabatic excitation energies, and anharmonic vibrational frequencies are computed for both the ground (\(\tilde{X}^2A''\)) and first excited (\(\tilde{A}^2A'\)) states using CC methods with perturbative triples or higher. The hydrogen, carbon, and oxygen atoms of CH₃O₂ were described by either \([H:4s3p2d1f], \, Li-Ne:[4s4p3d2f1g]; \, termed ANO2) or the truncated ANO1 basis set \([H:4s2p1d], \, Li-Ne:[4s3p2d1f]) [47]. ANO2 and ANO1 are of roughly quadruple-ζ and triple-ζ quality, respectively.

Anharmonic frequency values were obtained by appending anharmonic corrections (δν) determined with CCSD(T)/ANO1 to harmonic frequencies (ω) determined with CCSD(T)/ANO2. Second-order vibrational perturbation theory (VPT2) was employed to yield the anharmonic corrections, using analytic second derivatives at displaced geometries along the normal coordinates [48]. We have also included a correction for orbital relaxation (δω), which is calculated as the difference between CCSD(T)/ANO1 harmonic frequencies computed with Brueckner [49,50] and UHF reference determinants. For modes perturbed by a Fermi resonance, the offending terms were excluded from VPT2 analysis [51]; the correction for neglecting these terms was estimated using first-order couplings and included post facto [52,53]. VPT2 analysis was performed using PyVPT2 [54].

Optimised molecular geometries were obtained using CC theory with single, double, and perturbative triple excitations [CCSD(T)] [40–44] as implemented in CFOUR 1.0 [45]. Structural parameters were considered converged when the RMS force fell below \(10^{-9} \, E_h \, a_0^{-1}\). Unless otherwise noted, unrestricted Hartree–Fock (UHF) reference wavefunctions were employed. Convergence thresholds for the UHF density and CC amplitudes were both \(10^{-10}\). Minimum energy structures were confirmed after optimisation with harmonic vibrational frequency computations using analytic second derivatives [46]. The hydrogen, carbon, and oxygen atoms of CH₃O₂ were described by either \([H:4s3p2d1f], \, Li-Ne:[4s4p3d2f1g]; \, termed ANO2) or the truncated ANO1 basis set \([H:4s2p1d], \, Li-Ne:[4s3p2d1f]) [47]. ANO2 and ANO1 are of roughly quadruple-ζ and triple-ζ quality, respectively.
3. Results and discussion

3.1. Stationary points

Methyl peroxy radical possesses $C_s$ point-group symmetry, with the peroxy terminus trans to one of the hydrogen atoms (see Figure 2). We have determined the 0 K vibrationally averaged equilibrium geometries ($r_{g,0K}$) for the $\tilde{X}^2A^\ast$ and $\tilde{A}^2A'$ states using CCSD(T)/ANO2 with vibrational corrections predicted at CCSD(T)/ANO1. The $r_{g,0K}$ parameters were obtained by expanding each distance, $r$, in the leading terms of its normal coordinate Taylor expansion and averaging with respect to the ground vibrational state [73,74].

$$r_{g,0K} = \langle r \rangle_{0K} \approx r_e + \sum_s \left( \frac{\partial r}{\partial Q_s} \right)_e \langle Q_s \rangle_{0K} + \frac{1}{2} \sum_s \left( \frac{\partial^2 r}{\partial Q_s^2} \right)_e \langle Q_s^2 \rangle_{0K}.$$  \hspace{1cm} (1)

In Equation (1), the linear term, $\langle Q_s \rangle$, is averaged with respect to the VPT2 anharmonic vibrational wavefunction, whereas the quadratic term, $\langle Q_s^2 \rangle$, is averaged with respect to the harmonic vibrational wavefunction.

Compared to the ground state ($\tilde{X}^2A^\ast$), the first excited state ($\tilde{A}^2A'$) features a contracted C–O bond and an elongated O–O bond. This geometric difference reflects the fact that the ground and first excited states correlate with the $\tilde{X}^2\Sigma^-$ and $\tilde{a}^1\Delta_s$ states of $O_2$ at the C–O dissociation limit, where triplet $O_2$ has a shorter bond distance (1.208 Å) than singlet $O_2$ (1.216 Å). A convenient reference is the O–O bond in superoxide ($O_2^-$), which has the same bond order as $CH_3O=O$ but maintains the degeneracy of the $\pi$ orbitals on $O_2$. Its O–O bond distance of 1.348 Å lies between that of the ground (1.3252 Å) and first excited (1.4005 Å) states. Note that O–O elongation and R–O contraction is common to other peroxy radical systems, including $HO_2$ [36,75].

With regard to the $CH_3$ moiety, the in-plane $C$–$H$ bond remains essentially unchanged between the ground and first excited states, whereas the out-of-plane $C$–$H$ bonds are elongated by the $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$ transition. This 0.02 Å lengthening is a hyperconjugation effect in which doubly occupying the $3a''$ orbital, which is partially $\pi$-bonding over C–O, enhances the $p$-character of the $\pi_{CH_3}$ orbital. The barrier to torsional rotation of the methyl group is small – prior computational work suggests a value of 0.72 kcal mol$^{-1}$ [19].

3.2. Excitation energy and transition properties

To monitor $CH_3O_2$ using the vibronic $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$ transition, an accurate transition energy is required. To this end, several experimental investigations have refined this value, often employing theoretical work to confirm assignment. However, the theory data include computations that utilise a wide array of approaches, including density-functional and composite methods, which are not subject to systematic improvement or error assessment. In this work, we determine the transition energy using focal point analysis [56–59] in order to rigorously approach the correlation and basis set limits. Using this prescription we arrive at a transition energy within 9 cm$^{-1}$ of the best experimental value.

The data from our focal point analysis are shown in Table 1. At the CBS limit, contributions from full dou-
Table 1. Focal point extrapolation of the methyl peroxy radical $\tilde{X}^2A'^1 ← \tilde{X}^2A''$ excitation energy (in cm$^{-1}$) to the CBS limit of CCSDTQ. Corrections to the electronic energy are shown below the table (also see Theoretical methods).

| Method  | $\delta E$ CCSDTQ | $\delta E_{\text{SDT}}$ | $\delta E_{\text{SDTQ}}$ | $\delta E_{\text{SDT(T)}}$ | $\delta E_{\text{SDT(Q)}}$ | $\delta E_{\text{core}}$ |
|---------|-------------------|----------------------|-----------------------|----------------------|----------------------|-----------------|
| DZ      | 4609              | 2292                 | -4                    | 15                   | 42                   | -12             |
| TZ      | 4689              | 2313                 | -38                   | -1                   | 47                   | -12             |
| QZ      | 4741              | 2381                 | -40                   | -1                   | 47                   | -12             |
| S2      | 4747              | 2402                 | -44                   | -1                   | 47                   | -12             |
| 6Z      | 4748              | 2409                 | -45                   | -1                   | 47                   | -12             |
| CBS     | 4748              | 2417                 | -47                   | -1                   | 47                   | -12             |

$\Delta E_r = \Delta E_{\text{SDT}} + \Delta E_{\text{core}} + \Delta E_{\text{SDTQ}}$

$\Delta E_r = \Delta E_{\text{SDT}} + \Delta E_{\text{core}} + \Delta E_{\text{SDTQ}}$

Table 2. Comparison of $\tilde{X}^2A'^1 ← \tilde{X}^2A''$ transition origins ($T_0$) in cm$^{-1}$.

| Method  | $T_0$ (cm$^{-1}$) |
|---------|------------------|
| Ref. [11] | 7375 ± 6          |
| Ref. [13] | 7382 ± 0.5        |
| Ref. [17] | 7370 ± 40         |
| Ref. [16] | 7381 ± 1          |
| Ref. [12] | 7383              |
| Present work* | 7374              |

* See Table 1 and Theoretical methods.

Table 3. Vertical excitation energies ($\tilde{X}^2A''$), transition dipole moments ($\langle \hat{\mu} | \hat{A} \rangle$), and oscillator strengths ($f_A$) for the $\tilde{X}^2A'^1 ← \tilde{X}^2A''$ transition computed at the EOM-CCSD/ANO2 level of theory.

| $\tilde{X}^2A''$ | $\tilde{X}^2A'^1$ |
|------------------|------------------|
| Equilibrium      | Equilibrium      |
| $\tilde{X}^2A''$ | 8213 cm$^{-1}$   |
| $\tilde{X}^2A'^1$| 6494 cm$^{-1}$   |
| $\langle \hat{X} | \hat{\mu} | \hat{A} \rangle$ | 0.040 D          |
| $f_A$            | 6.3 $\times 10^{-6}$ |
| $\tau_A$         | 7.6 $\times 10^{-6}$ |

Note: $\tau_A = \frac{2\hbar}{\epsilon_0^2 \omega_0^2 \langle |\hat{\mu}|^2 \rangle}$

3.3. Anharmonic frequencies

Further spectral identification and assignment of CH$_3$O$_2$ using IR spectroscopy may be achieved through comparison with reported fundamental transitions. Indeed, there are several experimental investigations that report these values, but none that observe all 12 modes of the 12 modes that have been reported for the ground state, while only 3 of the 12 modes have been identified for the first excited state. In the latter case, the difficulty in preparing $\tilde{X}^2A'$ CH$_3$O$_2$ in the laboratory has limited analysis to those modes deduced from measuring the vibronic spectrum. This is a more complicated approach, since it involves disentangling spectra...
that contain excited vibrational frequencies on the $\tilde{X}^2A^\prime$ and $\tilde{A}^2A^\prime$ surfaces. To augment the available experiments, we predict the anharmonic frequencies for $\tilde{A}^2A^\prime$ CH$_3$O$_2$ here for the first time.

Our predictions are listed in Table 4. The final anharmonic values (ν) are a sum of the harmonic frequencies (ω), a correction for orbital relaxation (δω), and an anharmonic correction (δν). Anharmonic corrections were determined using second-order vibrational perturbation theory (VPT2) and coupled-cluster theory [CCSD(T)] with the ANO1 basis set. These corrections are less sensitive to the level of theory than the underlying harmonic frequencies, and are in general agreement with previous work on the ground state using CCSD(T)/cc-pVTZ [34]. To improve the quality of our predictions, harmonic frequencies were computed with the larger ANO2 basis and were corrected for deficiencies due to the UHF reference via Brueckner CC computations. The accuracy of this approach has been examined in prior work [3].

For the ground state ($\tilde{X}^2A^\prime$), we compare to five experimental reports: two argon matrix isolation investigations, one from Ase, Bock, and Snelson (1986) [20] and another from Ellison and co-workers (2002) [77]; two gas-phase studies, including work by Lineberger and co-workers (2001) [17] and Lee and co-workers (2007) [18]; and a recent He-matrix study by Douberly and co-workers (2012) [19]. The gas-phase and He-matrix values are most amenable to comparison with the present theoretical computations because they are least perturbed by environmental effects [78]. Compared to the values reported by Lee and co-workers [18], our predicted transitions differ on average by 5 cm$^{-1}$, and agreement with ν$_1$ is improved from our previous report (3026.7 vs. 3022 cm$^{-1}$) [34]. The largest disparity exists with ν$_6$ (11 cm$^{-1}$), but there is some disagreement

| Number | Sym | Description | ω (cm$^{-1}$) | δω (cm$^{-1}$) | ω (cm$^{-1}$) | δω (cm$^{-1}$) | v (cm$^{-1}$) | v (cm$^{-1}$) | v (cm$^{-1}$) | v (cm$^{-1}$) |
|--------|-----|-------------|---------------|----------------|---------------|----------------|---------------|---------------|---------------|---------------|
| v$_1$  | a'  | v$(\text{CH}_3)$ | 3174.9 ± 0.5 | -147.7 | 3026.7 (55) | 3033 ± 1 (100) | 3034.7 | 3032 |
| v$_2$  | a'  | v$(\text{CH}_3)$ | 3063.9 ± 0.5 | -107.6 | 2955.8 (90) | 2954 ± 1 (250) | 2955.5 | 2954 |
| v$_3$  | a'  | d$(\text{CH}_3)$ | 1497.0 ± 0.5 | -40.9 | 1455.6 (62) | 1453 ± 2 (100) | 1453 | 1448 (71) |
| v$_4$  | a'  | u$(\text{CH}_3)$ | 1450.3 ± 0.7 | -33.2 | 1416.5 (11) | 1408 ± 1 (54) | 1414 | 1410 (8) |
| v$_5$  | a'  | ρ$(\text{CH}_3)$/v$(\text{OO})$ | 1218.7 ± 1.4 | -31.4 | 1185.9 (70) | 1183 ± 1 (68) | 1183 | 1180 (37) |
| v$_6$  | a'  | ρ$(\text{CH}_3)$/v$(\text{OO})$ | 1167.7 ± 6.9 | -32.7 | 1128.1 (45) | 1117 ± 2 (74) | 1124 ± 5 | 1112 | 1109 (25) |
| v$_7$  | a'  | v$(\text{CO})$ | 947.5 ± 0.4 | -30.9 | 916.2 (100)$^a$ | 902 | 902 (78) |
| v$_8$  | a'  | δ$(\text{COO})$ | 484.4 ± 0.6 | -0.8 | 493.0 (46) | 482 ± 9 | 492 | 492 (30) |
| v$_9$  | a'' | v$(\text{CH}_3)$ | 3165.6 ± 0.2 | -148.2 | 3017.2 (79) | 3020 ± 2 (70) | 3024.5 | 3024 |
| v$_{10}$ | a'' | d$_1$(CH$_3$) | 1483.9 ± 0.4 | -43.1 | 1440.4 (60) | 1441 ± 1 (68) | 1440 | 1434 (100) |
| v$_{11}$ | a'' | ω$(\text{CH}_3)$ | 1145.7 ± 0.6 | -27.9 | 1117.2 (5.9) | 1145 | 1145 (91) |
| v$_{12}$ | a'' | ω$(\text{HCOO})$ | 150.5 ± 0.7 | -20.8 | 130.4 (0.8) | 150.5 | 150.5 (100) |

| Number | Sym | Description | ω (cm$^{-1}$) | δω (cm$^{-1}$) | ω (cm$^{-1}$) | δω (cm$^{-1}$) | v (cm$^{-1}$) | v (cm$^{-1}$) | v (cm$^{-1}$) | v (cm$^{-1}$) |
|--------|-----|-------------|---------------|----------------|---------------|----------------|---------------|---------------|---------------|---------------|
| v$_1$  | a'  | v$_6$(CH$_3$) | 3168.0 ± 0.4 | -147.0 | 3026.9 (9.2) | 3033 ± 1 (100) | 3034.7 | 3032 |
| v$_2$  | a'  | v$_6$(CH$_3$) | 3041.2 ± 0.6 | -92.5 | 2948.3 (44)$^b$ | 2954 ± 1 (250) | 2955.5 | 2954 |
| v$_3$  | a'  | d$_1$(CH$_3$) | 1519.5 ± 0.3 | -43.9 | 1475.3 (14) | 1453 ± 2 (100) | 1453 | 1448 (71) |
| v$_4$  | a'  | u$(\text{CH}_3)$ | 1454.5 ± 0.4 | -33.0 | 1421.2 (1.0) | 1408 ± 1 (54) | 1414 | 1410 (8) |
| v$_5$  | a'  | ρ$(\text{CH}_3)$ | 1185.7 ± 0.9 | -25.5 | 1159.3 (0.7) | 1183 ± 1 (68) | 1183 | 1180 (37) |
| v$_6$  | a'  | v$_6$(COO) | 1040.0 ± 2.5 | -29.2 | 1008.3 (100)$^b$ | 994 | 1002 | 1005 ± 10 |
| v$_7$  | a'  | v$_6$(COO) | 919.4 ± 7.1 | -2.3 | 910.0 (21) | 887 | 898 | 910 ± 10 | 896 ± 9 |
| v$_8$  | a'  | δ$(\text{COO})$ | 384.6 ± 0.9 | -4.3 | 379.4 (6.3) | 378 |
| v$_9$  | a'' | v$_6$(CH$_3$) | 3122.4 ± 0.4 | -147.0 | 2975.1 (36) | 2954 ± 1 (250) | 2955.5 | 2954 |
| v$_{10}$ | a'' | d$_1$(CH$_3$) | 1478.6 ± 0.5 | -39.6 | 1438.5 (11) | 1453 ± 2 (100) | 1453 | 1448 (71) |
| v$_{11}$ | a'' | ω$(\text{CH}_3)$ | 1177.9 ± 0.3 | -27.7 | 1149.9 (0.8) | 1145 | 1145 (91) |
| v$_{12}$ | a'' | ω$(\text{HCOO})$ | 248.9 ± 0.0 | -17.0 | 231.8 (1.9) | 248.9 | 248.9 (100) |

ν: stretch; δ: bend; τ: torsion; d: deformation; s: symmetric; a: asymmetric

$^a$Original value: 13.8 km mol$^{-1}$

$^b$Original value: 64.9 km mol$^{-1}$

$^c$Corrected for Fermi type I resonance ($2\omega_1 \approx \omega_2$); harmonic CCSD(T)/ANO2 intensity

$^d$Includes reassignments: v$_6$$\leftrightarrow$ v$_7$, v$_4$$\leftrightarrow$v$_{10}$, and v$_9$$\rightarrow$ v$_2$. See Refs [34, 77].
between the reported values for this mode: Lineberger and co-workers report 1124 cm$^{-1}$ [17] compared to Lee and co-worker’s value of 1117 cm$^{-1}$ [18], noting error bars of 5 and 2 cm$^{-1}$, respectively. Our predictions differ on average by 8 cm$^{-1}$ from the values for $\nu_6$ and $\nu_9$ reported by Lineberger and co-workers. With regard to the He-nanodroplet fundamentals observed by Douberly and co-workers, we find excellent agreement with $\nu_2 (< 1$ cm$^{-1}$), and qualitative agreement with $\nu_1$ and $\nu_6$, with our values shifted lower by 7–8 cm$^{-1}$. Overall, the close correspondence between our predicted transitions and the available data gives confidence in our computed frequencies for the first electronic excited state.

As discussed, only 3 of the 12 modes for $\tilde{A}$ $2A^\prime$ CH$_3$O$_2$ have been observed in experiments. These include cavity ring-down investigations by Miller and co-workers (2007) [12] and Hunziker and Wendt (1976) [11]; photoelectron spectroscopy from Lineberger and co-workers (2001) [17]; and a supersonic jet-expansion study by Fu, Hu, and Bernstein (2006) [16]. Beginning with the lowest reported frequency, $\nu_8$, we find excellent agreement (1 cm$^{-1}$) between our computed value (379.4 cm$^{-1}$) and the sole reported transition, that from Miller and co-workers (378 cm$^{-1}$) [12]. For $\nu_7$, there are four reported values ranging from 887 [12] to 910 cm$^{-1}$ [17] with an average of 898 cm$^{-1}$. Our prediction is 910.0 cm$^{-1}$. Finally, for $\nu_{6}$, the average reported value is 1000 cm$^{-1}$. We suggest a frequency for this transition of 1008.3 cm$^{-1}$.

4. Conclusions

Accurate characterisation of the methyl peroxy radical $\tilde{A}$ $2A^\prime$ ← $\tilde{X}$ $2A^\prime$ transition along with spectral data for both states is required for selective monitoring in kinetics experiments. We have determined the zero-point corrected geometries for the equilibrium structures on the ground ($\tilde{X}$ $2A^\prime$) and first excited ($\tilde{A}$ $2A^\prime$) states. Upon excitation, the O–O bond elongates concomitant with contraction of the C–O bond and lengthening of the out-of-plane C–H bonds. The latter effect is ascribed to hyperconjugation between $\pi_{CH_3}$ and $\pi_{O_2}$. We predict a transition energy of 7374 cm$^{-1}$ from extrapolation to the complete basis set limit at CCSDTQ, including anharmonic zero-point vibrational energies plus corrections to account for methodological approximations. This final theoretical $T_0$ value is within 9 cm$^{-1}$ of the best experimental results (7383 cm$^{-1}$); it has an estimated uncertainty of 15 cm$^{-1}$. Additionally, we predict Einstein $A$ (214 Hz) and $B$ (3.1 $\times$ $10^{16}$ m$^2$/J$^{-1}$s$^{-2}$) coefficients for spontaneous emission and for absorption, respectively. These data suggest a lifetime of $\tau_3 \approx 4.7$ ms for the excited state. Anharmonic vibrational frequencies are also reported for the ground and first excited states, the latter for the first time, using VPT2 theory and computations at the CCSD(T) level of theory with ANO basis sets. Our ground state values differ on average by approximately 5 cm$^{-1}$ from available gas-phase values, and good agreement is observed for the few available excited state transitions.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was supported by the Department of Energy, Office of Basic Energy Sciences [grant number DE-FG02-97-ER14748].

Supplemental data

Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/00268976.2015.1063729.

References

[1] J. Zador, C.A. Taatjes, and R.X. Fernandes, Prog. Energy Combust. 37, 371 (2011).
[2] C.K. Westbrook, Proc. Combust. Inst. 28, 1563 (2000).
[3] A.V. Copan, A.E. Wiens, E.M. Nowara, H.F. Schaefer, and J. Agarwal, J. Chem. Phys. 142, 054303 (2015).
[4] J.J. Orlando and G.S. Tyndall, Chem. Soc. Rev. 41, 6294 (2012).
[5] I.S. Ignatyev, Y. Xie, W.D. Allen, and H.F. Schaefer, J. Chem. Phys. 107, 141–155 (1997).
[6] B.J. Finlayson-Pitts and J.N. Pitts, Science 276, 1045 (1997).
[7] T.J. Wallington, P. Dagaun, and M.J. Kurylo, Chem. Rev. 92, 667 (1992).
[8] E.N. Sharp, P. Rupper, and T.A. Miller, Phys. Chem. Chem. Phys. 10, 3955–3981 (2008).
[9] P.D. Lightfoot, R.A. Cox, J.N. Crowley, M. Destriau, G.D. Hayman, M.E. Jenkin, G.K. Mooritgate, and F. Zabel, Atmos. Environ. 26A, 1805 (1992).
[10] B.G. Glover and T.A. Miller, J. Phys. Chem. A 109, 11191 (2005).
[11] H.E. Hunziker and H.R. Wendt, J. Chem. Phys. 64, 3488–3490 (1976).
[12] C.Y. Chung, C.W. Cheng, Y.P. Lee, H.Y. Liao, E.N. Sharp, P. Rupper, and T.A. Miller, J. Chem. Phys. 127, 044311 (2007).
[13] M.B. Pushkarasky, S.J. Zalyubovsky, and T.A. Miller, J. Chem. Phys. 112, 10695 (2000).
[14] D.B. Atkinson and J.L. Spillman, J. Phys. Chem. A 106, 8891 (2002).
[15] S. Wu, P. Duprê, P. Rupper, and T.A. Miller, J. Chem. Phys. 127, 224305 (2007).
[16] H.B. Fu, Y.J. Hu, and E.R. Bernstein, J. Chem. Phys. 125, 014310 (2006).
[17] S.J. Blanksby, T.M. Ramond, G.E. Davico, M.R. Nimlos, S. Kato, V.M. Bierbaum, W.C. Lineberger, G.B. Ellison, and M. Okumura, J. Am. Chem. Soc. 123, 9585–9596 (2001).
[18] D.R. Huang, L.K. Chu, and Y.P. Lee, J. Chem. Phys. 127, 234318 (2007).
[19] A.M. Morrison, J. Agarwal, H.F. Schaefer, and G.E. Douberly, J. Phys. Chem. A 116, 5299–5304 (2012).
[20] P. Ase, W. Bock, and A. Snelson, J. Phys. Chem. 90, 2099–2109 (1986).
[21] R.A. Bair and W.A. Goddard, J. Am. Chem. Soc. 104, 2719 (1982).
[22] S.L. Boyd, R.J. Boyd, and L.R. Barclay, J. Am. Chem. Soc. 112, 5724 (1990).
[23] W.D. Allen, D.A. Horner, R.L. Dekock, R.B. Remington, and H.F. Schaefer, Chem. Phys. 133, 11–45 (1989).
[24] S. Aloisio, Y. Li, and J.S. Francisco, J. Chem. Phys. 110, 9017–9019 (1999).
[25] A. Andersen and E.A. Carter, J. Phys. Chem. A 106, 9672–9685 (2002).
[26] J.A. Brandão, C.M.A. Rio, and J. Tennyson, J. Chem. Phys. 130, 134309 (2009).
[27] J.A. Jafri and D.H. Phillips, J. Phys. Chem. 106, 2590 (1990).
[28] M. Krauss and R. Osman, J. Phys. Chem. A 106, 2586 (1990).
[29] M. Kutzelnigg, Z. Phys. D 15, 287–290 (1990).
[30] G. Osmani, P. Bunker, P. Jensen, R. Bunker, J. Gu, and G. Hirsch, J. Mol. Spectrosc. 197, 262–274 (1999).
[31] C. Sousa, C. de Graaf, and G. Pacchioni, J. Chem. Phys. 114, 6259–6264 (2001).
[32] G.J. Vazquez, S.D. Peyerimhoff, and R.J. Buenker, Chem. Phys. 123, 11554–11559 (1992).
[33] J. Almlöf and P.R. Taylor, J. Chem. Phys. 84, 5761–5765 (1986).
[34] M.G. Delcey, R. Lindh, R. Llingeri, M. Hochlaf, and J.S. Francisco, J. Chem. Phys. 138, 021105 (2013).
[35] A. Li, D. Xie, R. Dawes, A.W. Jasper, J. Ma, and H. Guo, J. Chem. Phys. 133, 144306 (2010).
[36] J. Ma, H. Guo, C. Xie, A. Li, and D. Xie, Phys. Chem. Chem. Phys. 13, 8407–8413 (2011).
[37] V.V. Melnikov, T.E. Odaka, P. Jensen, and T. Hirano, J. Chem. Phys. 128, 114316 (2008).
[38] C. Xu, D. Xie, D.H. Zhang, S.Y. Lin, and H. Guo, J. Chem. Phys. 122, 244305 (2005).
[39] R.J. Bartlett and M. Musial, Rev. Mod. Phys. 79, 291 (2007).
[40] K. Raghavachari, G.W. Trucks, J.A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
[41] R.J. Bartlett, J.D. Watts, S.A. Kucharski, and J. Noga, Chem. Phys. Lett. 165, 513 (1990).
[42] J.F. Stanton, Chem. Phys. Lett. 281, 130 (1997).
[43] J.I.O. Deen and P.J. Knowles, Chem. Phys. Lett. 227, 321 (1994).
[44] CFOUR, a quantum chemical program package written by J.F. Stanton, J. Gauss, J.D. Watts, P.G. Szalay, R.J. Bartlett with contributions from A.A. Auer, D.E. Bernholdt, O. Christiansen, M.E. Harding, M. Heckert, O. Heun, C. Huber, D. Jonsson, J. Jusélius, W.J. Lauderdale, T. Metzroth, C. Michaulk, D.P. O’Neill, D.R. Price, K. Ruud, F. Schöffmann, A. Tafj, M.E. Varner, J. Vázquez and the integral packages: Molecule (J. Almlöf and P.R. Taylor), Props (P.R. Taylor), Abacus (T. Helgaker, H.J. Au, Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A.V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.
[45] P.G. Szalay, J. Gauss, and J.F. Stanton, Theor. Chem. Acc. 100, 5 (1998).
[46] J. Almlöf and P.R. Taylor, J. Chem. Phys. 86, 4070–4074 (1987).
[47] M.L. Mills, in Molecular Spectroscopy: Modern Research, edited by K.N. Rao and C.W. Matthews (Academic Press, New York, NY, 1972), Chap. 3.2, pp. 115–140.
[48] K. Brueckner, A. Lockett, and M. Rotenberg, Phys. Rev. 121, 255–269 (1961).
[49] J.F. Stanton, J. Gauss, and R.J. Bartlett, J. Chem. Phys. 97, 5554–5559 (1992).
[50] A.V. Copan Jr, D.A. Clabo, R.B. Remington, Y. Yamaguchi, and H.F. Schaefer, Chem. Phys. 123, 187 (1988).
[51] H.H. Nielsen, Phys. Rev. 68, 181 (1945).
[52] J.M.L. Martin, T.J. Lee, P.R. Taylor, and J.P. François, J. Chem. Phys. 103, 2589 (1995).
[53] PyVPT2 is a vibrational anharmonicity program written in Python by J. Agarwal. Center for Computational Quantum Chemistry, University of Georgia, Athens, GA.
[54] M. Källay and P.R. Surján, J. Chem. Phys. 115, 2945–2954 (2001).
[55] W.D. Allen, A.L.L. East, and A.G. Császár, in Structures and Conformations of Non-Rigid Molecules, edited by J. Laane, M. Dakkouri, B. Veenk, and H. Oberhammer (Kluwer Academic Publishers, Dordrecht, Netherlands, 1993), Chap. 10, pp. 343–373.
[56] A.L.L. East and W.D. Allen, J. Chem. Phys. 99, 4638–4650 (1993).
[57] A.G. Császár, W.D. Allen, and H.F. Schaefer, J. Chem. Phys. 108, 9751–9764 (1998).
[58] M.S. Schuurman, S.R. Muir, W.D. Allen, and H.F. Schaefer, J. Chem. Phys. 120, 11586–11599 (2004).
[59] D.E. Woon and T.H. Dunning, J. Chem. Phys. 103, 4572–4585 (1995).
[60] W. Kutzelnigg, Z. Phys. D 11, 15–28 (1989).
[61] W. Kutzelnigg, Z. Phys. D 15, 27–50 (1990).
[62] H. Sellers and P. Pulay, Chem. Phys. Lett. 103, 463–465 (1984).
[63] M.S. Schuurman, W.D. Allen, and H.F. Schaefer, J. Comput. Chem. 26, 1106–1112 (2005).
[64] J.F. Stanton and R.J. Bartlett, J. Chem. Phys. 98, 7029–7039 (1993).
[65] J.F. Stanton, Annu. Rev. Phys. Chem. 59, 433 (1998).
[66] J.M. Turney, A.C. Simmonett, R.M. Parrish, E.G. Hohenstein, F.A. Evangelista, J.T. Fernmann, B.J. Mintz, L.A. Burns, J.J. Wilke, M.L. Abrams, N.J. Russ, M.L. Leininger, C.L. Janssen, E.T. Seidl, W.D. Allen, H.F. Schaefer, R.A. King, E.F. Valeev, C.D. Sherrill, and T.D. Crawford, WIREs Comput. Mol. Sci. 2, 556 (2012).
[67] Z. Rolik, L. Szegedy, I. Ladjánszki, B. Lődőczki, and M. Källay, J. Chem. Phys. 139, 094105 (2013).
[68] K. Kuchitsu, in Accurate Molecular Structures: Their Determination and Importance, edited by A. Domenico and I. Hargittai (Oxford University Press, Oxford, UK, 1992), Chap. 2, pp. 14–43.
[69] A.G. Császár, in Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry, edited by J. Demaison, J.E. Boggs, and A.G. Császár (CRC Press, Boca Raton, FL, 2011), Chap. 8, pp. 233–262.
[70] R.P. Tuckett, P.A. Freedman, and W.J. Jones, Mol. Phys. 37, 403 (1979).
[71] G.M.P. Just, A.B. McCoy, and T.A. Miller, J. Chem. Phys. 127, 044310 (2007).
[72] S. Nandi, S.J. Blanksby, X. Zhang, M.R. Nimlos, D.C. Dayton, and G.B. Ellison, J. Phys. Chem. A 106, 7547 (2002).
[73] M.E. Jacox, Acc. Chem. Res. 37, 727 (2004).