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Geometry of the $CaOCH_3$ radical from isotope effects in the $\tilde{A}^2E$–$\tilde{X}^2A_1$ transition

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Abstract

The analysis of laser excitation spectra of the $\tilde{A}^2E$–$\tilde{X}^2A_1$ origin band of the $CaOCH_3$ radical reported in 2002 [J. Mol. Spectrosc. 213 (2002) 28] left some geometric parameters undetermined. Working with isotopically substituted methoxy groups, with ^{12}C or ^{13}C and complete D/H substitution, we have recorded the origin bands and the 4_0^1 band of the $\tilde{A}$–$\tilde{X}$ system of four isotopomers of calcium monomethoxide. The rotational constants derived from the analysis of the spectra are used in a fit to determine bond lengths and angles in the two electronic states.

Keywords: Laser excitation spectroscopy; Isotope effects; Isotopic substitution; Symmetric top; Laser ablation; $CaOCH_3$; Alkaline-earth compounds

1. Introduction

In a recent publication [1] we reported an analysis of high resolution spectra of the $\tilde{A}^2E$–$\tilde{X}^2A_1$ transition of $CaO^{12}CH_3$. The molecules were formed in a laser ablation source by reacting methanol with calcium vapour produced by ablating a calcium rod with the pulsed UV radiation from the third harmonic of a Nd:YAG laser. We analysed the spectra and estimated the molecular geometry, but because there were four structural parameters (three bond lengths and the H $\hat{C}$ H angle) and only two rotational constants, B and A, it was not possible to determine unique structural parameters. The only conclusions we could draw were that there was a decrease in the Ca–O bond length on excitation from the $\tilde{X}$ to the $\tilde{A}$ state and that the CH_3 "umbrella" did not change significantly. Previous analyses of data for the $\tilde{B}^2A_1$–$\tilde{X}^2A_1$ transition [2] had fixed the O–C and C–H bond lengths to values obtained from OCH_3 [3] and methanol [4], respectively, and had then determined the Ca–O bond length and the H $\hat{C}$ H bond angles for the $\tilde{X}$ and $\tilde{B}$ states.

We have now obtained high resolution excitation spectra of the $\tilde{A}$–$\tilde{X}$ transition in four separate calcium monomethoxide isotopomers, $CaO^{12}CH_3$, $CaO^{12}CD_3$, $CaO^{13}CH_3$, and $CaO^{13}CD_3$ by using different varieties of isotopically substituted methanol. From the complete set of rotational constants it should be possible to determine most of the structural parameters uniquely, and also to determine the effects (if any) of electronic excitation and isotopic substitution on the geometry of the methyl group. The experimental details were identical to those previously described [1].

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2. Spectra and analysis

We obtained high resolution spectra of the 0_0^0 origin band for all four isotopomers. We also obtained spectra of the 4_0^1 band in which the υ_4 Ca–OCH_3 stretching vibration was excited in the $\tilde{A}$ state. A portion of the spectrum of the $\tilde{A}^2E_{1/2}$–$\tilde{X}^2A_1$ component of the origin band of each isotopomer is shown in Fig. 1. It can be seen that there is a small red shift of $<0.1\ cm^{-1}$ when ^{13}C is substituted for ^{12}C, and a much larger shift of $\sim 10\ cm^{-1}$ on substituting D for H. All four isotopomers showed a similar structure to that described in [1], and for the two hydride species, comparison of the spectra enabled the lines to be assigned in a straightforward manner. Because of their increased moments of inertia about both *a* and *b* axes, the deuteride spectra were more compact and their assignment was more challenging. However, careful use of combination differences allowed us to make assignments that were internally consistent. The range of quantum numbers covered by our observations is given in Table 1. The data for the main isotopomer are by far the most complete (we only had small samples of isotopically substituted methanol). A complete list of observed lines and their assignment has been deposited in the Journal archives.

The techniques and programs that were used to fit the data are described in detail in [1]. We used the Hamiltonian of Endo et al. [3] and Cerny et al. [5] to calculate the energies of the upper ^2E and lower $^2A_1$ states, respectively. The fitting of the data was done in several stages. In the first iteration, the data for each isotopomer were fitted to the same set of upper-state parameters considered in our first paper [1]. The ground-state constants for the main isotopomer $CaO^{12}CH_3$ were fixed at the values used in our original study [1], which had been obtained with microwave accuracy [6]. All other parameters were optimized, and the results examined for isotopic consistency. As the experimental conditions allowed us to observe only low *K* values ($|K| \leqslant 2$ in most cases) in the rotational levels and modest *N* (typically $N'' < 25$), the $\Delta K = +1$, $\Delta N = 0, \pm 1$ selection rules mean that while the B' and B'' rotational constants should be well defined by the spectra, only the difference ΔA can be obtained, and distortion terms would not easily be extracted.

When fitting the data, we began with ground-state *A* values for the hydride species that were initially fixed at previous values [1]. The ground-state *A* values for the deuterides were made isotopically consistent using the ratio $A_D/A_H = m_H/m_D$. It was found that several of the smaller distortion and spin rotation parameters showed large random variations between the isotopomers, and were not very well determined. Because of correlation effects, these do have a small effect on the B values, and would therefore affect subsequent structural calculations.

In the next iteration, the ground-state parameters for $CaO^{12}CH_3$ were again fixed, and the distortion and spin

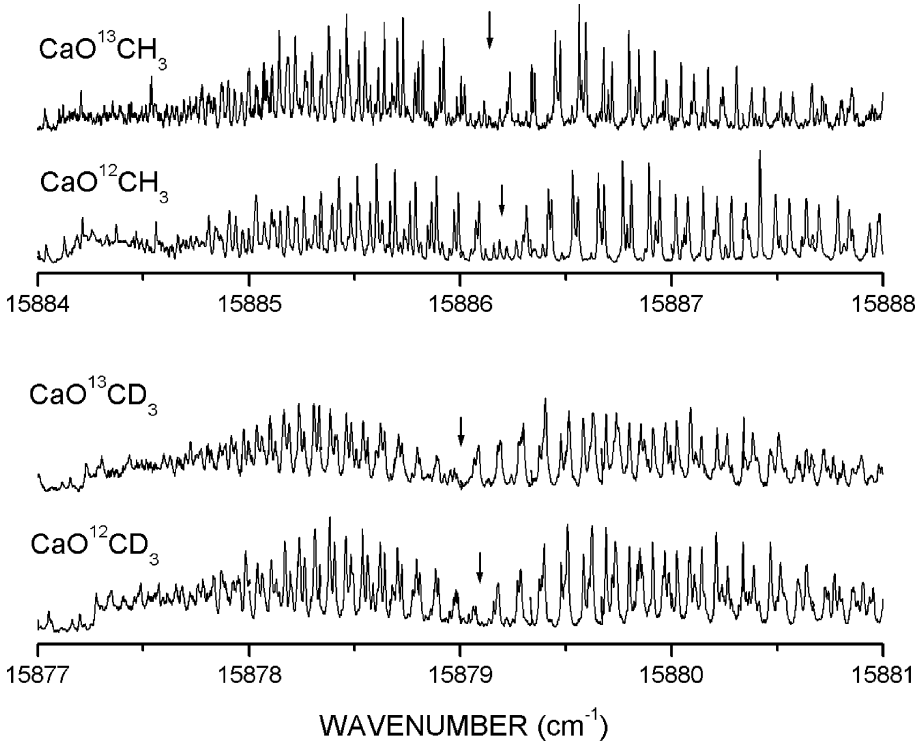

Fig. 1. A portion of the $\tilde{A}^2E_{1/2}$–$\tilde{X}^2A_1$ component of the origin band of calcium monomethoxide for four different isotopomers showing the effect of H/D and $^{12}C/^{13}C$ substitution on the band origin region. The arrows show the positions of the sub-band origins.

Table 1
Data included in the fits

Isotopomer	Number of lines 0_0^0 band	Number of lines 4_0^1 band	N''_{max}	K''_{max}	RMS error (cm^{-1}) in least-squares fit
$CaO^{12}CH_3$	514	330	35	3	0.0028
$CaO^{13}CH_3$	433	443	22	2	0.0033
$CaO^{12}CD_3$	374	413	20	2	0.0034
$CaO^{13}CD_3$	374	400	21	3	0.0042

rotation parameters for the other isotopomers were fixed at values that were isotopically consistent, leaving the rotational constant B'' as the only ground-state parameter to be determined when the data were refitted. We removed the ground-state distortion coefficient D_K which previously had been fixed [1] at a value determined with microwave accuracy for $CaOCH_3$ [6], and whose contribution to all line wavenumbers was less than the experimental uncertainty.

In a third iteration, the upper-state distortion constants D_N were made the same for both vibrational levels, and were fixed at values that were isotopically consistent with the well-determined value for the $v = 0$ level of the main isotopomer. Some of the smaller terms which made no significant contribution to the line wavenumbers were also removed at this stage. In this final fit, the ground-state A values were changed to values that were consistent with the structure calculations (see below), but as only ΔA could be determined from the fit, this made no difference to the final results. The various adjustments had no significant effect on the overall RMS deviation of the fits ($\sim$0.003 cm^{-1}), and the final results, presented in Tables 2 and 3 for the ground and upper states, give a minimal set of parameters that are

Table 2
Spectroscopic parameters (cm^{-1}) for the $\tilde{X}^2A_1$ ground state of the calcium monomethoxide radical

Parameter	$CaO^{12}CH_3$	$CaO^{13}CH_3$	$CaO^{12}CD_3$	$CaO^{13}CD_3$
B	0.11626490(3)[a,c]	0.1125480(44)	0.1015093(56)	0.0989430(66)
10^8 D''_N	2.688	2.52	2.05	1.95
10^6 D''_{NK}	2.358	2.281	1.030	1.003
A''	5.3748[b]	5.3748[b]	2.6895[b]	2.6895[b]
10^4 ε''_{bc}	4.153	4.020	3.626	3.534

[a] Determined at microwave accuracy by Namiki et al. [6].
[b] Iteratively determined from geometry parameters, see Table 4.
[c] The number in parentheses indicates 1 standard deviation error, in units of last digit.

Table 3
Parameters (cm^{-1}) for the $\tilde{A}^2E$ state of the calcium monomethoxide radical

Parameter	$CaO^{12}CH_3$	$CaO^{13}CH_3$	$CaO^{12}CD_3$	$CaO^{13}CD_3$
T[a]	15925.0482(3)[b]	15924.9727(3)	15915.1877(4)	15915.0947(5)
	16426.5271(4)	16420.3353(3)	16396.8122(3)	16391.9231(4)
A	5.36701(7)	5.3671(1)	2.6850(1)	2.6854(2)
	5.36713(4)	5.3665(1)	2.6854(1)	2.6854(7)
B	0.117888(1)	0.1140953(47)	0.1028934(60)	0.1002800(70)
	0.117489(2)	0.1137201(44)	0.1025819(57)	0.0999745(66)
10^8 D_N	2.47(15)	2.31	1.88	1.79
	2.5	2.31	1.88	1.79
$a\zeta_e d$	66.9736(4)	66.9673(3)	66.8414(5)	66.8393(7)
	67.0872(5)	67.0810(5)	66.9550(4)	66.9540(4)
$A\zeta_t$	5.3644(1)	5.3639(2)	2.6832(2)	2.6834(2)
	5.3643(3)	5.3635(1)	2.6835(1)	2.6829(1)
10^3 ε_1	−8.20(1)	−8.00(3)	−7.09(4)	−6.93(5)
	−8.19(3)	−8.060(3)	−7.11(4)	−6.76(7)
10^3 ε_{aa}	2.32(33)	2.2	4.54(43)	3.63(60)
	3.35(45)	2.22(36)	3.41(28)	3.63
10^4 h_1	1.44(12)	1.35	1.10	1.04
	1.44	1.35	1.10	1.04
v'_4[c]	501.479	495.362	481.625	476.828

[a] The upper value in each row corresponds to $v' = 0$ (i.e., the zero-point level for the upper state), and the lower value for $v'_4 = 1$.
[b] The number in parentheses indicates 1 standard deviation error, in units of last digit.
[c] Vibrational wavenumbers (v'_4) are the differences between the two upper state term energies for each species.

well determined, are isotopically consistent, and in which correlation effects have been minimized. A and B are the usual inertial rotational constants, the D terms are distortion coefficients, ε_1, ε_{aa}, ε_{bc} are fine structure constants, $a\zeta_e d$ represents the spin–orbit coupling in the ^2E state, and $A\zeta_t$ the Coriolis coupling.

3. Geometrical structure

The rotational patterns observed in our $\tilde{A}^2E$–$\tilde{X}^2A_1$ spectra correspond to a C_{3v} molecular geometry. This confirms the conclusions of previous investigations [1,2], that the Ca–O–C backbone of this molecule is linear (or has a very low barrier to linearity). Four structural parameters define the geometry of the calcium methoxide radical, namely the vibrationally averaged (R_0) bond distances R_{CaO}, R_{OC}, and R_{CH} and bond angle θ_{HCH} (or θ_{OCH}). In trying to determine these parameters, we found that the C–H bond length and OCH bond angle are totally correlated. The B values are sensitive primarily to R_{CaO}, R_{OC} and the axial component of R_{CH}, $(R_{CH})_z$, while the A values are sensitive only to the orthogonal component, $(R_{CH})_y$. As we can only determine a *change* in A from our spectra, it is still not possible, even with our abundance of isotopic information, to determine the CH_3 structure uniquely.

In principle we should be able to do better, as the B value does, in fact, also depend on A. It can be shown that the moment of inertia about the b axis is $I_b = I_{b\,(\mathrm{linear})} + 0.5I_a$, where $I_{b\,(\mathrm{linear})}$ is the moment of inertia of an equivalent linear molecule CaOCX in which X would be a hypothetical atom of mass $3m_H$ ($3m_D$) placed at the CX distance $(R_{CH})_z$ where the H or D atoms project onto the symmetry axis; I_a represents the moment of inertia about the symmetric top axis in the three-dimensional molecule. This equation can be written in terms of rotational constants, giving $1/B = 1/B_{(\mathrm{linear})} + 1/(2A)$. Thus, by fitting to B values for four isotopomers, we should in principle be able to determine the four structural parameters. However, because A is ~50 times larger than B, its contribution to the I_b moment of inertia is very small and its isotopic variation is tiny. As a result, the values obtained for the C–H bond length and angle are very poorly determined. The isotopic data do enable us to determine a value for $(R_{CH})_z$, but a reliable A value is still needed to determine the perpendicular component $(R_{CH})_y$, and hence to give reliable estimates of both the bond length and bond angle.

The structural parameters were determined using an approach in which the values of B', B'', and ΔA for the various isotopomers were all fitted simultaneously. The input data were weighted according to their standard deviations (see Tables 2 and 3), and the ground-state C–H bond length was fixed at the methanol value of 1.0937 Å [4]. R_{CD} was assumed to be $0.99806 \times R_{CH}$ in both the ground and the excited state, where the factor 0.99806 is based on the experimental B_0'' values for CH_4 and CD_4 quoted by Hollenstein et al. [7]. The output from the fit gave optimized values of the ground-state structural parameters, of their changes on excitation, and realistic estimates of the associated parameter uncertainties. The fit also automatically rounds the parameters in a manner which retains sufficient digits to reproduce the data without significant loss of precision [8]. In an effort to reduce the effect of inter-parameter correlation, the fitting parameters used to characterize the structure in the $\tilde{A}^2E$ excited state were actually the *changes* in the bond lengths and angle relative to those for the ground state. Preliminary fits also found that changes in the O–C and C–H bond lengths and in the OCH angle determined from spectra of the 0_0^0 and 4_0^1 bands were identical (within their uncertainties) for the $v_4' = 0$ and 1 levels of the $\tilde{A}$ state. Hence, the changes in those bond lengths and bond angle were constrained to be the same for the two $\tilde{A}$ state vibrational levels in the final fit which yielded the results shown in Table 4. The dimensionless root mean square residual of this fit is 1.65.

In this final fit there remained a particularly high degree of correlation between the changes in the C–H bond length and the OCH bond angle, and between the changes in the Ca–O bond length in the $v_4' = 0$ and 1 levels of the $\tilde{A}$ state (correlation coefficients of

Table 4
Structural parameters for the $\tilde{X}^2A_1$ and $\tilde{A}^2E$ states of the calcium monomethoxide radical[a]

Parameter	X state ($v'' = 0$)	Change on excitation to $\tilde{A}^2E$	
		$v' = 0$	$v_4' = 1$
Ca–O bond length (Å)	1.9623418 (±0.0042)[b]	−0.020407 (±0.0055)	−0.015213 (±0.0055)
O–C bond length (Å)	1.4106 (±0.0065)	0.0 (±0.009)	
C–H bond length (Å)	1.0937[c]	−0.0014 (±0.0016)	
O–C–H angle (°)	111.3 (±0.2)	−0.2996 (±0.21)	

All parameters were rounded while retaining sufficient digits to ensure no loss of precision in the representation of the input spectroscopic constants [8].

[a] The dimensionless root mean square residual for the fit is 1.65.

[b] The uncertainties given in parentheses indicate 68% confidence limits.

[c] Tabulated R_0 value for methanol, taken from [4].

0.9999). Indeed, for all eight fitted structural parameters, the statistical uncertainties (which include the effects of correlation) shown in Table 4 are 2–3 orders of magnitude larger than the uncertainties obtained if only one parameter is fitted at a time. However, if either the C–H bond length or the OCH bond angle is not allowed to change on electronic excitation, the quality of fit becomes somewhat worse, with dimensionless root mean square residuals of 1.78 and 1.90, respectively, but the change in the other parameter appears to become very well determined, ($\Delta\theta_{OCH} = -0.111(1)^\circ$ if $\Delta R_{CH} = 0$, or $\Delta R_{CH} = +0.000814(7)$ Å if $\Delta\theta_{OCH} = 0$). On the other hand, if no change at all is allowed in the structure of the methyl group in the excited electronic state, the fit becomes very poor (a dimensionless root mean square residual of 37!), since this imposes $\Delta A = 0.0$. Thus, it is clear that almost all of the uncertainty in the fitted structural parameters presented in Table 4 is due to inter-parameter correlation.

There is also very strong correlation between the Ca–O and O–C bond distances in the ground state (correlation coefficient 0.9986). However, while the change in the Ca–O bond length on electronic excitation is moderately well determined ($\sim -0.020(6)$ Å for $v_4' = 0$ and $\sim -0.015(6)$ Å for $v_4' = 1$), that of the O–C bond length is very poorly determined, with an uncertainty of greater than 100%, and the automatic rounding procedure [8] makes it identically zero ($\sim 0.0 \pm 0.009$ Å) without significantly affecting the quality of the overall fit.

4. Vibrations

Although the main goal of this work was to determine the geometric structure of the molecule, Table 3 allows us to make a preliminary examination of the effect of isotopic substitution on the Ca–OCH_3 stretching frequency in the $\tilde{A}^2E$ state. The vibrational spacings between the $v_4' = 0$ and 1 levels are given in Table 3 for the four isotopomers. The ratios of the vibrational spacings on isotopic substitution are 1.04 (H/D) and 1.01 ($^{12}C/^{13}C$). From low resolution spectra, Wormsbecher and Suenram [9] found the same H/D ratio for the ground-state υ_4 vibrational spacing, whose value for the hydride was $\sim 13\ cm^{-1}$ smaller than that for the $\tilde{A}$ state. Using this information, we can predict that the origin band will be shifted by $\sim 0.25\ cm^{-1}$ to lower wavenumber on substitution of H by D, and by $\sim 0.077\ cm^{-1}$ for the ^{12}C to ^{13}C substitution, due to the isotope effect on the Ca–OCH_3 stretching vibration. This effect can account for the observed $0.075\ cm^{-1}$ separation of the origin bands of the two carbon species, but certainly cannot explain the observed $9.9\ cm^{-1}$ shift between those for the hydrogen and deuterium species. Our spectra do not explain this effect, but preliminary experiments have shown that this shift does not occur in the $\tilde{B}^2A_1$–$\tilde{X}^2A_1$ transition, so it would appear that the shift is symmetry dependent.

5. Discussion

The main objective of this work was to establish directly the geometrical structure of $CaOCH_3$, removing the need to fix the bond lengths at values previously obtained for similar molecules such as $SrOCH_3$ [10], $CaCH_3$ [11], and OCH_3 [3,12], and to see whether we can provide a better determination of the effect of electronic excitation on the geometry of the CH_3 group. In their paper on the $\tilde{B}$–$\tilde{X}$ transition, Whitham et al. [2] had fixed the O–C bond length at the value of 1.376 Å obtained by Endo et al. [3] for the OCH_3 radical, while our results indicate that in $CaOCH_3$ this bond is stretched slightly to 1.4106(65) Å (our value is slightly smaller than the bond length 1.4246(24) Å reported for methanol [13]). However, the present study shows that the O–C bond length does not change significantly on electronic excitation to the $\tilde{A}$ state.

In order to obtain an estimate of the Ca–O bond length, Whitham et al. had also fixed the overall CH_3 geometry to be the same as that in OCH_3, thereby obtaining values of 1.9945 Å for the ground state and 1.9730 Å for the $\tilde{B}$ state. Our results give a distinctly shorter Ca–O bond length of 1.9623(42) Å for the ground state, and show that it decreases by 0.0204(55) Å on excitation to the $v_4' = 0$ level of the $\tilde{A}$ state and by 0.0152(55) Å on excitation to $v_4' = 1$. Thus, there seems to be a similar shortening of this bond on excitation to both the $\tilde{A}$ and $\tilde{B}$ states. We note that the uncertainties in our $\tilde{A}$ state Ca–O bond length changes may seem fairly large. However, if we repeat the fit reported in Table 4 while applying the one additional constraint that the Ca–O bond length change in $v_4' = 0$ and 1 be the same, the resulting dimensionless residual becomes 41.6. Thus the present analysis very clearly shows both that the Ca–O bond length shrinks on excitation to the $\tilde{A}$ state, and that this bond length shrinkage becomes distinctly smaller with vibrational excitation in the $\tilde{A}$ state.

The effects of electronic excitation and isotopic substitution on the geometry of the CH_3 group are harder to determine. Our fits indicate that with the ground-state C–H bond length fixed at 1.0937 Å, the O $\hat{C}$ H bond angle is 111.3(2)°, giving an H $\hat{C}$ H angle of 107.6(2)°. The results in Table 4 indicate that the change in this structure due to electronic excitation is very small. The bond length decreases by 0.0014(15) Å and the O $\hat{C}$ H angle by 0.3(2)° to 111.0(2)°. The large relative uncertainties in these changes are mainly due to interparameter correlation, and neglect of any changes leads to an unacceptably high dimensionless RMS deviation for the fit.

The details of this change in CH_3 geometry are obviously not very well determined, but if we examine how the RMS deviation of the fit changes with fixed trial values of the change $\Delta\theta$ in the OCTT angle, it is clear that reasonable fits can be obtained only when $\Delta\theta$ is negative, indicating a small opening of the CH_3 umbrella on excitation. In terms of the H $\hat{C}$ H angle, this indicates an increase from 107.6° to 107.9°.

From the ΔA values for the hydride and deuteride species, it should in principle be possible to determine whether the isotopic substitution affects the geometry of the CH_3 group beyond the small fixed relative decrease in R_{CH} included in our model. If the CH and CD R_0 distances were equal, and the angle also invariant, the ratio of the ΔA values would be the inverse of the ratio of the hydrogen and deuterium masses. We find that the values of $\Delta A(CH_3)$ calculated from the values of $\Delta A(CD_3)$ differ from the fitted values by an amount that is slightly greater than the experimental uncertainties. It is difficult to read much significance into this, except to say that if there is a change in the excited-state CH_3 structure on isotopic substitution, it is less than 0.0001 Å in the bond length and/or less than 0.01° in the bond angle.

Because our spectra do not allow us to determine A directly, it has not been possible to determine the full geometric structure of $CaOCH_3$ without having to fix one of the structural parameters associated with the geometry of the CH_3 group. Since most previous determinations of structure for this and similar molecules lacked adequate isotopic data, it had been necessary to fix both the bond length and angle of this group. In contrast, in the present work, isotopic substitution has allowed us effectively to determine all the on-axis bond lengths in the ground state, and their changes with electronic and vibrational excitation. As in many previous studies of OCH_3 [3], $SrOCH_3$ [10], and $CaOCH_3$ [2], we chose to fix the ground-state C–H bond length at the methanol value of 1.0937 Å. In some similar studies this bond length was fixed at larger values, ranging up to 1.122 Å [6], the ab initio value calculated for the methoxy anion CH_3O^- [14]. It is therefore important to examine what effect changes in the assumed C–H bond length have on our results. We found that changing the C–H bond length to 1.122 Å increases our value for the ground-state Ca–O bond length by only 0.0007 Å and decreases the O–C bond length by only 0.0009 Å, changes almost an order of magnitude smaller than our estimated parameter uncertainties (see Table 4).

The behaviour of the CH_3 group on electronic excitation has been studied for several molecules. In most cases, the C–H bond length in the excited state was fixed at the ground-state value and the change in the H $\hat{C}$ H angle was determined. Our isotopic analysis indicates a slight shortening (by ~0.0014 Å) of the C–H bond and a simultaneous small increase in the H $\hat{C}$ H bond angle of ~0.3°. Although both of these changes have large estimated uncertainties (see Table 4), we believe the direction, if not the actual magnitude of these changes, to be real. When we fixed the $\tilde{A}$-state C–H bond length at the ground-state value of 1.0937 Å, the H $\hat{C}$ H bond angle increased by ~0.11° and the dimensionless RMS deviation increased by 8%, to 1.78.

A fairly large range of H $\hat{C}$ H bond angles are quoted in the literature for different molecules, but the associated uncertainties are not reported in most cases. For OCH_3 the angle reported was ~110° [3,12], and the same value was obtained for $SrOCH_3$ [10] from an analysis in which A'' was fixed at the OCH_3 value. The H $\hat{C}$ H bond angle was found to be ~109.20° for $ZnCH_3$ and $CdCH_3$ [5]. Brazier and Bernath [11] give H $\hat{C}$ H = 105.6(±2.8)° in the X state of $CaCH_3$, and 109.2(±3)° in the $\tilde{A}$ state, from analysis of electronic spectra. These values depend not only on the value of A, but also on the value chosen for the C–H bond length. For example, Endo et al. [3] used 1.0937 Å for OCH_3, while Liu et al. [12] used 1.10 Å. This difference changes the associated bond angle by ~1°.

Of even more significance is the change in this bond angle with electronic excitation. For OCH_3 the bond angle increased by 4° [12], and for $ZnCH_3$ and $CdCH_3$ it increased by just over 3° [5], with estimated uncertainties of 2–4°. For $SrOCH_3$ a decrease of 2.7° was quoted for the H$\hat{C}$H angle [10]. However, on recalculating the H$\hat{C}$H angles using the quoted A values, we found that the angle quoted for the $\tilde{A}$ state of $SrOCH_3$ was actually the H$\hat{C}$O angle, and that there was, in fact, an *increase* of ~0.5° in the H$\hat{C}$H angle, a change which is consistent with our results for $CaOCH_3$.

The bonding in $CaOCH_3$ is ionic (Ca^+–$^-OCH_3$). Previous papers [2,10] have described an effect known as anionic hyperconjugation, which predicts [15] that in the CH_3O^- ion, the O^- donates electrons into the unoccupied $p\pi^*$ orbital on the carbon atom, an interaction which makes the O–C bond shorter in the ion than in the neutral OCH_3 radical. Our observation that the O–C bond length is 0.032 Å *longer* in $CaOCH_3$ than in OCH_3 indicates that the Ca^+ ion tends to pull the O^- away from the CH_3 group, thus lengthening the O–C bond, which suggests that the hyperconjugation model does not apply here. Although our multiple isotopomer analysis has shown that the Ca–O bond length is 0.03 Å shorter than was estimated in previous work [2], the ~0.02 Å decrease in this bond length on electronic excitation to the $\tilde{A}$ state is the same as that observed for similar transitions in CaOH [16] and $SrOCH_3$ [10], as well as that for the $\tilde{B}$–$\tilde{X}$ transition in $CaOCH_3$ [2].

6. Conclusions

Isotopic substitution has enabled us to determine structural parameters in the $\tilde{X}^2A_1$ ground state and in

the $\tilde{A}^2E$ first excited electronic state of the $CaOCH_3$ molecule from an analysis which involves fixing only one parameter, the ground-state C–H bond length. These results show that the O–C bond length in $CaOCH_3$ is longer than that in the OCH_3 radical, and that it does not change significantly on excitation to the $\tilde{A}$ state. The Ca–O bond length is slightly shorter than was previously thought and decreases by $\sim$0.02 Å on excitation to the $\tilde{A}$ state, an effect similar to that observed in similar molecules. The determination of the CH_3 structure is more difficult because of the lack of a well-defined experimental A value, and we regretfully conclude that our determination of its structure is dependent on the choice of a fixed parameter, the ground-state C–H bond length. Isotopic substitution allowed us more flexibility than was possible in previous studies, and although the associated statistical uncertainties are relatively large, our results seemed to indicate a very slight shortening of the C–H bond and opening of the CH_3 umbrella on excitation from the $\tilde{X}$ to the $\tilde{A}$ state. However, an unambiguous definition of the CH_3 structure will require a direct determination of the A rotational constant, perhaps through observation of a perturbation similar to that seen in $CaCH_3$ [11].

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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