# **RSC Advances**



CrossMark

Cite this: RSC Adv., 2015, 5, 40856

Received 21st February 2015 Accepted 29th April 2015 DOI: 10.1039/c5ra03255e

www.rsc.org/advances

# 1 Introduction

Alkanes, including cycloalkanes, are released into the atmosphere from a variety of anthropogenic sources.1-3 Their oxidation leads to the formation of the alkoxy radicals which are key intermediates and cause secondary pollutants (e.g., ozone, aldehydes, ketones, aerosols), and thus contributes to the degradation of air quality in and around urban regions. The spectroscopy of the smallest alkoxy radicals is well studied, with detailed spectral analyses having been reported for CH<sub>3</sub>O<sup>4,5</sup> and C<sub>2</sub>H<sub>5</sub>O.<sup>6</sup> In 2001, Carter et al. have systematically reported the jet-cooled, moderate resolution LIF spectra from all of the 1alkxoy,  $C_n H_{2n+1}O$ , radicals with n = 3 through 10.<sup>7</sup> Subsequently, Gopalakrishnan and co-workers reported the analyses of the rotational structure in the high-resolution spectra of a number of bands of 1-propoxy.8 Two different conformers of 1propoxy were assigned based upon similarity of rotational structure. The spectrum of each conformer abruptly terminated after the excitation of a single C-O stretch. At the same year, Gopalakrishnan et al. reported the rotationally resolved spectra of bands of 1-butoxy and 1-pentoxy radicals as the number of skeletal carbon atoms increased.9 As expected, the highresolution spectra of 1-butoxy was ascribable to three different

# LIF excitation spectrum of cyclohexylmethoxy and 2-cyclohexylethoxy

Qijun Wu,\*<sup>ac</sup> Hongyan Zhang,<sup>a</sup> Xun Gong\*<sup>b</sup> and Fengjun Zhang<sup>c</sup>

1-Alkoxy and its cyclohexyl substituted variants play an important role in atmospheric chemistry. Spectroscopic and conformational studies can provide convenient methods to monitor these species and help to understand the reaction mechanism in the atmosphere. In this work, we report the LIF excitation spectrum following photolysis of cyclohexylmethyl and 2-cyclohexylethyl nitrites. The rotationally resolved LIF formaldehyde spectrum appeared in the narrow wavelength region of 28 290 to 28 350 cm<sup>-1</sup> in the photolysis precursor cyclohexylmethyl and 2-cyclohexylethyl nitrites. Furthermore, for the first time, a nicely resolved vibrational structure LIF spectrum of 2-cyclohexylethoxy was acquired in the wavelength region of 28 800 to 29 800 cm<sup>-1</sup>. This spectrum was assigned preliminarily to  $G_1G_2$  and  $G_1G'_2$  conformers of 2-cyclohexylethoxy. The spectrum of 2-cyclohexylethoxy was similar to 1-propoxy that no  $\nu > 1$  C–O stretch was observed in the jet-cooled spectrum. By a combination of experimental spectrum and computational results, we can learn the stabilization effects depending on molecular geometry, due to the substitution of the  $\alpha$  H of CH<sub>3</sub>O and  $\beta$  H of CH<sub>3</sub>CH<sub>2</sub>O by the big cyclohexyl group.

conformers, however 1-pentoxy showed the present of six different conformers. In 2004, rotationally resolved spectra of 1hexoxy were obtained and assigned four conformers for five vibronic bands, and two conformers for three vibronic bands of 1-heptoxy.10 It is summarized the primary alkoxy radicals  $(C_n H_{2n+1}O)$  with  $3 \le n \le 7$  that appear three bands persistently, labeled bands A, B and C. Band A has been assigned as the origin of the  $G_1T_2...T_{n-2}$  conformer ( $C_1$  symmetry), while bands B and C are, respectively, the origin and CO stretch fundamental of conformer  $T_1T_2...T_{n-2}$  with  $C_s$  symmetry. 1-Octoxy, 1nonoxy and 1-decoxy would also expect the pattern to continue in even larger alkoxy radical. Many larger alkoxy radicals can have multiple structural isomers which increase dramatically as the number of skeletal carbon atoms increase. As a complexity for multiple conformations, the spectroscopy of primary alkoxy radicals substituted by cyclohexyl has not been so welldeveloped.

Cyclohexane exists the possibility of chair and boat conformer.<sup>11</sup> However, X-ray and electron diffraction experiments clearly prove the cyclohexane exists almost exclusively in the chair conformation, which is devoid of any kind of strain.<sup>12</sup> Several pathways is also possible in which the chair can undergo inversion is through a planar cyclohexane ring. Our approach, studying the jet-cooled LIF spectrums of cyclohexylmethoxy and 2-cyclohexylethoxy are important to reveal the stereodynamic effect of cyclohexyl, which substitute  $\alpha$  H atom of methoxy and  $\beta$  H atom of ethoxy, respectively. The result will contribute to the fundamental chemical and structure investigation of 1-alkoxy derived from cyclohexyl.



View Article Online

View Journal | View Issue

<sup>&</sup>quot;School of Chemical Engineering, Guizhou Institute of Technology, Guiyang 550003, China. E-mail: wuqijun1981@mail.bnu.edu.cn

<sup>&</sup>lt;sup>b</sup>School of Light Industry, Guizhou Institute of Technology, Guiyang 550003, China. E-mail: gongxunplmm@163.com

<sup>&</sup>lt;sup>c</sup>School of Chemical Engineering, Guizhou University of Engineering Science, Bijie 551700, China

#### Paper

In this work, we obtained the jet-cooled LIF spectrum of cyclohexylmethoxy and 2-cyclohexylethoxy radical and analyzed the spectrum assisted by theoretical calculations using B3LYP/ 6-31+G(d) and CASSCF/6-31+G(d) methods. The conformation identity of the spectrum was discussed, and the spectral and chemical property of cyclohexylmethoxy and 2-cyclohexylethoxy radical was compared with primary ethoxy and 1-propoxy radicals.

# 2 Experimental

The experimental setup was described previously in ref. 13. Briefly, it consists of a dye laser (Narrowscan, Radiant Dyes) pumped by the second harmonic (532 nm) of a Nd:YAG laser (Continuum, Surelite III). The laser output was frequencydoubled to generate the UV radiation required to probe the  $\tilde{B}$ - X electronic transition of cyclohexylmethoxy and 2-cyclohexylethoxy. Photolysis of the precursor molecules (the scheme for RCH<sub>2</sub>ONO +  $h\nu \rightarrow$  RCH<sub>2</sub>O' + NO) were achieved the corresponding alkoxy radicals using the third harmonic (355 nm) of another Nd:YAG laser (Continuum, Surelite II), with power of typically 30 mJ per pulse. The cyclohexylmethyl and 2-cyclohexylethyl nitrites precursor were synthesized by dropwise addition of sulfuric acid to a mixture of alkyl alcohols and sodium nitrite.14 The cyclohexylmethyl and 2-cyclohexylethyl nitrites appeared as pale yellow liquid, which were verified by IR and UV spectra.15 A backing pressure of ~0.1 atm argon passed over the nitrite sample and the resulting gaseous mixture was expanded into the vacuum chamber using a standard pulse valve (General Valve) with a 0.5 mm orifice. The photolysis beam was focused just above the throat of the nozzle, and the radicals produced were excited about 10 mm downstream by the counter-propagating probe beam. The total fluorescence was collected perpendicularly with a f = 80 mm lens and imaged onto a photomultiplier tube (Hamamasu, CR110). The valve was operated in a continuous mode. The vacuum chamber was evacuated by a molecular pump (600 L s<sup>-1</sup>) backed by a mechanical pump (8 L s<sup>-1</sup>). The initial vacuum was  $\sim 3 \times 10^{-3}$ Pa and increased to  $\sim$ 7 Pa when injecting sample.

Two dyes, Pyridine 2 and Pyridine 1 (Exciton, USA), were used to provide the tunable excitation laser source for cyclohexylmethoxy and 2-cyclohexylethoxy LIF spectra. Lasers were operated at 10 Hz rate and sequentially controlled by a Digital Pulse Generator (Stanford Research, DG535). The output of the photomultiplier was digitized on an oscilloscope (Tektronics, TBS3032B) and the gated signal was integrated by a LabVIEW program. LIF spectra were obtained by recording the integrated fluorescence signal while continuously scanning the excitation laser wavelength. The dye laser wavelength was scanned at 0.01 nm per step and all spectra were corrected by subtracting the background obtained with the photolysis laser off.

# 3 Computational

The geometry optimization at ground state of all conformers of alkoxy radical was performed using B3LYP/6-31+G(d) method. The CASSCF/6-31+G(d) method was used to optimize the

geometries of the ground state and  $\tilde{B}$  excited state of all alkoxy radical. An active space of 9 electrons distributed in 7 orbitals was chosen in the CASSCF method, involving the two nonbonding orbits of O atom (HOMO and HOMO–1, in which the HOMO is half-filled), the  $\sigma$  (HOMO–2) and  $\sigma^*$  (LUMO) orbitals of the C–O bond, and other active orbitals and electrons automatically chosen by the program. Vibrational frequency analysis was conducted for the ground and excited states to assist the assignment of experimental spectra. The adiabatic excitation energy between  $\tilde{X}$  and  $\tilde{B}$  states was obtained by CASSCF/6-31+G(d) method.

The geometry optimizations and frequency analysis were performed to identify the minima and transition states. The transition structures for possible decomposition and isomerization reaction of the corresponding radical were further optimized by the synchronous transit-guided quasi-Newton (STQN) method, and intrinsic reaction coordinate (IRC) calculations were conducted to find the respective the reactant and first guess product on the potential energy surface to which the transition state connected. All calculations were performed using Gaussian 03 program.

### 4 Experimental results

#### 4.1 LIF experimental spectra

In the range 28 000–30 000 cm<sup>-1</sup>, the LIF excitation spectrums following photolysis of the primary cyclohexylmethyl and 2cyclohexyethyl nitrites, was showed in Fig. 1. The nicely resolved vibrational structure LIF spectrum of 2-cyclohexylethoxy appeared in the wavelength region of 28 800 to 29 700 cm<sup>-1</sup> in Fig. 1(b), is similar excitation region for the primary alkoxy radicals ( $C_nH_{2n+1}O$ ) with  $3 \le n \le 10$ . The only rotationally resolved LIF spectrum appeared in the narrow wavelength region of 28 290 to 28 350 cm<sup>-1</sup> in the photolysis precursor cyclohexylmethyl nitrites, was enlarged in the right rectangle region in Fig. 1(a). The same magnifying LIF spectrum was also obtained for the precursor 2-cyclohexylethyl nitrite, in a



**Fig. 1** Jet-cooled LIF excitation spectrum following photolysis (355 nm) of the primary cyclohexylmethyl and 2-cyclohexyethyl nitrites: (a) LIF spectrum of formaldehyde; (b) LIF spectrum of 2-cyclohexylethoxy and formaldehyde.

Table 1Zero-point energies (ZPE) of alkoxy radical, transition states(TS), and reaction products for isomerization (isom.) and decomposition (decomp.)

Species		$E + ZPE (ref)^a$ (kcal mol <sup>-1</sup> )
$C_{6}H_{11}CH_{2}CH_{2}O'(G_{1}G_{2})$		0.0
isom. $(C_3-H\cdots O)$	TS	15.6
	Product	3.9
Decomp.	TS	13.6
1	Product	9.6
$C_{6}H_{11}CH_{2}CH_{2}O'(G_{1}G'_{2})$		0.22
isom. $(C_4 - H \cdots O)$	TS	9.92
	Product	0.42
Decomp.	TS	13.72
1	Product	9.62
$C_6H_{11}CH_2CH_2O'(T_1G_2)$		0.45
Decomp.	TS	14.25
1	Product	9.65
C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub> O'		0.0
Decomp.	TS	11.7
····	Product	8.2

<sup>a</sup> Relative energies with zero-point energy (ZPE) corrections.

relatively weak intensity. The identical rotational resolved spectrum is the same upon excitation of formaldehyde in supersonic jet<sup>16,17</sup> and flames.<sup>18,19</sup> The producing RO from the photolysis primary alkyl nitrites undergoes a C–C scission to yield an alkyl radical and formaldehyde.

The cyclohexylmethoxy and 2-cyclohexylethoxy radical were generated by replacing the hydrogen atom on the  $\alpha$ ,  $\beta$  carbon of methoxy and ethoxy with cyclohexyl group, respectively. The relative energies of cyclohexylmethoxy and 2-cyclohexylethoxy (the three lowest energy conformers following the detailed conformational analysis section) radicals, transition states, and products are given in Table 1. The calculation results showed the barriers of the transition structure and ground state of cyclohexylmethoxy radical in C–C bond fission is favor to 1.8 kcal mol<sup>-1</sup> lower in energy than 2-cyclohexylethoxy radical, in a B3LYP/6-31+G(d) calculation level. As for our experiment and calculation result, the big cyclohexyl group substituent the  $\alpha$  carbon of methoxy suggested to be the cause of the reduced barrier to decomposition compare to  $\beta$  carbon of ethoxy.

#### 4.2 Conformational analysis of 2-cyclohexylethoxy radical

The conformational analysis of cyclohexane and its substitutes was well addressed in the literature.<sup>20</sup> It is known that there are two types of conformer for cyclohexoxy, chair form and twisted-boat form. The twisted-boat conformers are ~6 kcal mol<sup>-1</sup> higher in energy than chair conformers.<sup>13,21</sup> Therefore, only chair conformers are likely present under our experimental conditions. For 2-cyclohexylethoxy radicals, cyclohexyl group can be treated as the substitute the hydrogen atom on the  $\beta$  carbon of ethoxy. The two different isomers can exist according to the axial (chair-a) or equatorial (chair-e) position of cyclohexyl that the ethoxy group take. The each isomer has 5 unique conformers of 2-cyclohexylethoxy radicals in the ethoxy group

Paper

structural isomers. Theoretical calculation showed that chair-a conformer is at least 0.79 kcal mol<sup>-1</sup> higher in energy than the chair-e conformers. This is consistent with the stability studies of cyclohexane and its substitutes in the paper.<sup>21</sup>

The general method for analytically determining the number of conformers of primary alkoxy radicals has already been described in 1-butoxy paper,9 and can be extended to 2-cyclohexylethoxy. In 2-cyclohexylethoxy, cyclohexyl in a chair-e conformation has a  $C_s$  symmetry, there are two pairs of threebond sets, that is, C2-C1-O with C1-C2-C3 and C1-C2-C3 with  $C_2-C_3-C_4$  or  $C_2-C_3-C'_4$  ( $C_3-C_4$  and  $C_3-C'_4$  bond of cyclohexyl on adjacent C<sub>2</sub> atom) that can form two dihedral angles  $\Phi_1$  and  $\Phi_2$  $(\Phi'_2)$ . As cyclohexyl in a chair-e conformation has a  $C_s$  symmetry, the  $\Phi_2$  and  $\Phi'_2$  are their mirror images, we consider the only one of the  $\Phi_2$  and  $\Phi'_2$ . The two dihedral angles  $\Phi_2$  and  $\Phi'_2$  are illustrated in the Newman diagrams of Fig. 2(a). If we consider the first structure shown in Fig. 2(a), which has  $C_s$  symmetry as a reference structure, then rotation about the C<sub>1</sub>-C<sub>2</sub> bond changes the value of the angle  $\Phi_1$  with three values expected to correspond to staggered minima, as shown in the first row of Fig. 2(a). The three structures are designated  $T_1$ ,  $G_1$ , and  $G'_1$ , respectively, for trans, gauche clockwise, and gauche counterclockwise for the C1-C<sub>2</sub> torsion. We can also rotate about the C<sub>2</sub>-C<sub>3</sub> bond to obtain different values of the angle  $\Phi_2$  with again three staggered minima expected, as shown in the second row of Fig. 2(a). These are analogously designated  $T_2$ ,  $G_2$ , and  $G'_2$  for the  $C_2$ - $C_3$  torsion. Because the values of  $\Phi_1$  and  $\Phi_2$  are independent, they can be combined to form a total of nine conformers. The conformer corresponding to  $T_1T_2$  has  $C_s$  symmetry and is unique. Of the remaining eight conformers, four are unique and the others are their mirror images (indicated in parentheses), that is,  $T_1G_2$  $(T_1G'_2), G_1T_2, (G'_1T_2), G_1G_2, (G'_1G'_2), and G_1G'_2, (G'_1G_2).$  The unique conformers are pictured in Fig. 2(b).

The  $G_1G_2$ ,  $G_1G'_2$  and  $T_1G_2$  conformers, rotation about the  $C_1$ - $C_2$  bond changes the value of the angle  $\Phi_1$  with three values expected to correspond to staggered minima, as the minima relative ground energies of 2-cyclohexylethoxy radical below 0.45 kcal mol<sup>-1</sup>. The three relative energies of conformers and barriers between conformers of 2-cyclohexylethoxy radical at the ground state were calculation at the B3LYP/6-31+G(d) level, as shown in the Fig. 3.

The  $G_1G_2$  and  $T_1G_2$  conformers are 0.22 and 0.45 kcal mol<sup>-1</sup> higher in the Zero-Point Energies (ZPE) than the minimal energy G1G2 conformers respectively. The barrier from the G1G'2 to the  $G_1G_2$  conformer are 3.30 kcal mol<sup>-1</sup>, while the barriers from  $G_1G_2$  conformers to  $G_1G'_2$  conformer are 3.52 kcal mol<sup>-1</sup>. The same, the barriers from the T<sub>1</sub>G<sub>2</sub> to the G<sub>1</sub>G<sub>2</sub> conformer are 1.74 kcal mol<sup>-1</sup>, while the barriers from  $G_1G_2$  conformers to  $T_1G_2$  conformers are 2.19 kcal mol<sup>-1</sup>. The energy barrier between  $G_1G'_2$  and  $T_1G_2$  conformers is lower than 1.80 kcal  $mol^{-1}$ . Thus,  $G_1G_2$  conformers are easy to convert to  $T_1G_2$ , then convert to G<sub>1</sub>G'<sub>2</sub>, while the high barriers make the interconversion direct from G<sub>1</sub>G<sub>2</sub> conformer to G<sub>1</sub>G'<sub>2</sub> conformer difficult. These calculation results suggest that G1G2 conformers are the first favor present under the jet-cooled experimental condition.11,22 Therefore, we can analyze the LIF spectrum using calculated results of chair conformers.





Fig. 2 Value (a) for 2-cyclohexylethoxy of the dihedral angles  $\Phi_1$  and  $\Phi_2$  (staggered) for which local minima occur and structures (b) of five unique conformers of 2-cyclohexylethoxy corresponding to the combination of angles  $\Phi_1$  and  $\Phi_2$  at their local minima.

However the existence of the very different rotational structures in ref. 22 confirms the presence of multiple species contributing to the spectrum. As for the 2-cyclohexlethoxy



Fig. 3 Potential energy curve of interconversion between  $G_1G_2,\,G_1G_2'$  and  $T_1G_2$  conformers of 2-cyclohexylethoxy at the ground state.

radical, we will ordinal favor to the lowest energy of  $G_1G_2$ ,  $G_1G'_2$  and  $T_1G_2$  conformers for assigning the observed vibrational bands, under the jet conditions.

#### 4.3 Excitation state analysis of the 2-cyclohexlethoxy

Due to the lower symmetry ( $C_s$  or  $C_1$ ) of 2-cyclohexlethoxy radical, the doubly degenerate ground state of methoxy radical is split into two close lying ( $\tilde{X}$  and  $\tilde{A}$ ) quasi-degenerate states.<sup>23</sup> The lowest three electronic states  $\tilde{X}$ ,  $\tilde{A}$  and  $\tilde{B}$  of alkoxy radicals were well defined in literature.<sup>21,23,24</sup> The study of alkoxy radicals has revealed that the  $\tilde{B} - \tilde{X}$  electronic transition is essentially the excitation of an electron from the C–O  $\sigma$  orbital to the halffilled p– $\pi$  orbital localized on the oxygen atom.<sup>11,25</sup>

The CASSCF (9,7)/6-31+G(d) calculations show that the vibrational modes and their frequencies are very similar for the  $G_1G_2$ ,  $G_1G'_2$  and  $T_1G_2$  conformers of 2-cyclohexlethoxy radical. Table 2 lists calculated lowest 20 vibrational frequencies of the three conformers (in lower symmetry  $C_1$ ). The B3LYP/6-31+G(d)

and CASSCF (9,7)/6-31+G(d) calculations both show C–O stretch vibrations (below  $\nu_{47}$ ) at over 900 cm<sup>-1</sup> for the G<sub>1</sub>G<sub>2</sub>, G<sub>1</sub>G'<sub>2</sub> and T<sub>1</sub>G<sub>2</sub> conformers on the ground state. In the  $\tilde{B}$  excited state, significantly low C–O stretch frequencies, 570 cm<sup>-1</sup> ( $\nu_{54}$ ) for G<sub>1</sub>G<sub>2</sub> conformer, 555 cm<sup>-1</sup> ( $\nu_{54}$ ) for G<sub>1</sub>G'<sub>2</sub> conformer, and 622 cm<sup>-1</sup> ( $\nu_{54}$ ) for T<sub>1</sub>G<sub>2</sub> conformer, were predicted (Table 2). Moreover, the G conformer of 1-propoxy was assigned at 596 cm<sup>-1</sup> above the original band as likely corresponding predominantly to the excitation of the C–O stretch.<sup>8</sup> This value is quite consistent with  $\omega_0$  of 603 cm<sup>-1</sup> for the C–O stretch in C<sub>2</sub>H<sub>5</sub>O.<sup>26</sup>

#### 4.4 Spectroscopy study

The LIF spectrum of 2-cyclohexylethoxy taken in supersonic jet condition is shown in Fig. 1(b). The spectrum appears in the wavelength region of 28 800–29 800 cm<sup>-1</sup>. Assigning the vibrational bands of 2-cyclohexlethoxy spectrum is difficult because of the closely energy of the three lowest conformers and the rich vibrational modes of the radicals. However, previous studies of chain and cyclic alkoxy radicals can provide good starting ground. First, the conformer which was calculated to be lowest in energy had always been designed priority for all alkoxy

Vibration mode	$G_1G_2$			$G_1G'_2$			$T_1G_2$		
	$CASSCF(9,7)^b$		B3LYP	$CASSCF(9,7)^b$		B3LYP	$CASSCF(9,7)^b$		B3LYP
	Ĩ	ñ	Ĩ	Ĩ	Ñ	Ĩ	Ĩ	Ñ	Ĩ
<i>v</i> <sub>66</sub>	39	41	51	22	51	62	67	73	76
$\nu_{65}$	83	80	85	114	104	98	71	77	81
$v_{64}$	158	153	162	120	122	123	114	116	122
$\nu_{63}$	203	197	199	217	203	220	173	180	188
$\nu_{62}$	220	221	230	231	219	228	217	218	227
$\nu_{61}$	298	299	313	248	276	282	269	282	301
$\nu_{60}$	316	313	325	321	323	334	307	311	322
$\nu_{59}$	384	390	350	368	386	400	331	340	354
$\nu_{58}$	410	405	413	402	409	427	418	424	441
$\nu_{57}$	427	419	430	429	426	444	426	427	444
$\nu_{56}$	469	429	447	471	475	491	441	453	472
$\nu_{55}$	518	510	522	518	517	536	536	552	572
$\nu_{54}$	570	566	550	555	735	770	622	671	678
$\nu_{53}$	730	742	776	752	774	797	747	759	788
$\nu_{52}$	776	775	800	774	788	831	774	775	798
$\nu_{51}$	800	805	848	797	818	844	779	818	852
$\nu_{50}$	816	813	849	815	833	860	818	832	856
$\nu_{49}$	867	853	897	860	860	889	858	864	900
$\nu_{48}$	883	870	908	881	886	919	867	896	928
$\nu_{A7}$	888	896	933	886	906	938	903	905	935

<sup>a</sup> All calculations employed the 6-31+G(d) basis set. <sup>b</sup> A uniform scale factor of 0.9 was used for CASSCF frequencies.

Fable 3	Assignment of the bands (in cm	$^{-1}$ ) observed in the low-	-frequency region	of the jet-cooled LIF	<sup>=</sup> spectrum of 2	2-cyclohexylethoxy radical
---------	--------------------------------	--------------------------------	-------------------	-----------------------	----------------------------	----------------------------

Band Exp		Δexp		Predicted, G <sub>1</sub> G <sub>2</sub>		Predicted, G <sub>1</sub> G' <sub>2</sub>	
	Expt freq	$\Delta \exp^a$	$\Delta \exp^b$	Freq <sup>c</sup>	Assign	Freq <sup>c</sup>	Assign
A	28 935.6	0		0	$\nu_{00}^{B-X}$		
В	28 987.0	51		39	v <sub>66</sub>		
С	29 042.0	106		83	$\nu_{65}$		
D	29 051.2	116	(0)			0	$\nu_{00}^{\mathrm{B-X}}$
Е	29 068.0	132	(17)			22	$\nu_{66}$
F	29 123.4	188		203	$\nu_{63}$		
G	29 160.3	225	(109)			114	$\nu_{65}$
Н	29 215.7	280		298	ν <sub>61</sub>		
I	29 488.2	553		570	ν <sub>54</sub> C-O		
J	29 568.4	633	(517)			518	$\nu_{55}$
K	29 596.0	660	(545)			555	ν <sub>54</sub> C–O

<sup>*a*</sup> Observed band maxima (cm<sup>-1</sup>) relative to  $G_1G_2 \nu_{00}^{B-X}$  at 28 935.6 cm<sup>-1</sup>. <sup>*b*</sup> Observed band maxima (cm<sup>-1</sup>) relative to  $G_1G_2 \nu_{00}^{B-X}$  at 29 051.2 cm<sup>-1</sup>. <sup>*c*</sup> Scaled CASSCF(9,7)/6-31+G(d) frequencies (scale factor 0.90).

radicals reported.<sup>22</sup> Secondly, the C–O stretch mode is expected to have high intensity in the LIF spectrum since the  $\tilde{B} - \tilde{X}$  transition of alkoxy radicals corresponds to the promotion of one electron from the  $\sigma$  orbital of the C–O bond to the half-filled non-bonding orbital that mainly localized on O atom.<sup>23,25</sup>

The results of the assignment of experimental vibronic bands A through I of 2-cyclohexylethoxy in Table 3 establish the presence of two different conformers and identify the bands by theoretical computational method. A similar behavior was observed that for both of the G and T conformers of 1-propoxy the LIF spectrum abruptly terminates at  $\leq$ 700 cm<sup>-1</sup> above its origin with only one quantum of C–O stretch observed. Thus, the spectrum can be considered to be established that bands A, B, C, F, H and I correspond to the G<sub>1</sub>G<sub>2</sub> conformer and bands D, E, G, J and K to the G<sub>1</sub>G'<sub>2</sub> conformer of 2-cyclohexylethoxy.

Let us first consider the vibrational structure of spectrum of  $G_1G_2$  conformer. The origin band (band A) is at 28 935.6 cm<sup>-1</sup>, which is blue-shifted compared to the origin band of 1-propoxy (28 634.2 cm<sup>-1</sup>). Band I, 553 cm<sup>-1</sup> above the origin band in the experiment spectrum, fits well with the predicted C–O stretch vibration frequency ( $\nu = 570 \text{ cm}^{-1}$ ) of the  $G_1G_2$  conformer. The weaker band B, C, F, and H can be assigned as  $\nu_{66}$  (torsion between  $C_2$ – $C_1$ –O and cyclohexyl),  $\nu_{65}$  (bend between  $C_2$ – $C_1$ –O and cyclohexyl),  $\nu_{61}$  (whole C–C–O backbone deformation, CH<sub>2</sub> rock in  $\alpha$  carbon),  $\nu_{61}$  (whole C–C–O backbone stretch), respectively (Table 3).

Bands D (116 cm<sup>-1</sup>), J (633 cm<sup>-1</sup>) and K (660 cm<sup>-1</sup>), above the origin band A, whose intensity are higher compared to the C–O stretch vibration for band I. These bands were not predicted by  $G_1G_2$  conformer calculations. Therefore, the spectral observation leads to the possibility of coexistence of other conformers in the experimental condition. If band D is assigned as the origin of the  $G_1G'_2$  conformer, the high intensity band K in the spectrum can be assigned as  $\nu_{54}$  (C–O stretch) of  $G_1G'_2$ conformer with the discrepancy ~2%. Bands E, G and J can be assigned as  $\nu_{66}$  (torsion between C<sub>2</sub>-C<sub>1</sub>-O and cyclohexyl),  $\nu_{65}$ (whole C–C backbone bend),  $\nu_{55}$  (whole C–C backbone stretch) of the  $G_1G'_2$  conformer, respectively. On the other hand, combinations vibrational mode of band C and band I (C–O stretch) of the  $G_1G_2$  conformer is located at band J position. Thus, band J have a higher intensity in C–C backbone stretch of  $G_1G'_2$  conformer for the Fermi Resonance Effect. Calculated vibrational frequencies are shown in Fig. 4 for comparing with the experimental data. Detail assignments are listed in Table 3.

The CASSCF (9,7) adiabatic excitation energy between  $\tilde{X}$  and  $\tilde{B}$  states of  $G_1G'_2$  conformer was 31 156 cm<sup>-1</sup>, which was 106  $cm^{-1}$  in high frequency direction of  $G_1G_2$  conformer. It was a little difference for 6 cm<sup>-1</sup> by the CIS method. This difference of the two chair conformers in vertical excitation was 567 cm<sup>-1</sup> as calculated by TDDFT method. Although the uncertainty of the calculated excitation energy is probably the magnitude of several hundred wavenumbers,27 the general conclusion we can draw from the calculation results is that the origin band of  $G_1G'_2$  conformer should appear to the high frequency side of  $G_1G_2$  origin if  $G_1G'_2$  conformer is present in the jet. This calculation result supports our assignment in Table 4. Coexistence of multiple conformers was observed previously by rotationally resolved spectroscopy study in the non-equilibrium jetcooled experimental condition of chain alkoxy radicals, for example, gauche (G) and trans (T) conformers of 1-propoxy,<sup>8</sup>  $G_1T_2$ ,  $T_1T_2$  and  $T_1G_2$  conformers of 1-butoxy.<sup>9</sup> At current stage, the two-conformer assignment of 2-cyclohexlethoxy spectrum has best agreement between experimental and calculation



Fig. 4 Assignment of experimental spectrum with calculated vibrational frequencies of  $G_1G_2$  (red) and  $G_1G'_2$  (blue) conformers. Unified intensity was used for all calculated vibration modes except the C–O stretch vibrations.

	TDDFT/6-31+G(d)		CIS/6-31+G(d)		CASSCF(9,7)/6-31+G(d)	
Conformer	$\tilde{A}-\tilde{X}$	$\tilde{B}-\tilde{X}$	$\tilde{A}-\tilde{X}$	$\tilde{B}-\tilde{X}$	$\tilde{B}-\tilde{X}$	
$G_1G_2$	2519	27 795	1863	33 893	31 050	
$G_1G'_2$	3033	28 362	1794	33 899	31 156	

Table 4Calculated excitation energies (in cm<sup>-1</sup>) of the  $G_1G_2$  and  $G_1G'_2$  conformers of 2-cyclohexlethoxy radical (vertical excitation energy byTDDFT method, adiabatic excitation energy by CIS and CASSCF method, respectively.)

results. An unambiguous assignment requires further studies of rotationally resolved spectroscopy.

The lower  $C_1$  symmetry for  $G_1G_2$  conformers of 2-cyclohexlethoxy give rise to the ground X and a low-lying A state. For a given 1-alkoxy conformer, T1 or G1 near the oxygen atom, increasing the alkyl chain decreases the  $\tilde{A} - \tilde{X}$  separation.<sup>28</sup> Experimental and calculated  $\tilde{A} - \tilde{X}$  energy separation of 1-propoxy are 214 and 8 cm<sup>-1</sup>, respectively.<sup>28</sup> The  $\tilde{A} - \tilde{X}$  separation of isopropoxy is  $\sim 60 \text{ cm}^{-1}$  using new electronic structure calculations and rotational contour analyses.<sup>29</sup> A weaker band a (Fig. 4) is 26.7  $\text{cm}^{-1}$  to the low frequency side of band A in our experimental spectrum, which we attributed to transitions to the  $\tilde{B}$  state from the low-lying  $\tilde{A}$  electronic state for  $G_1G_2$ conformers. The vertical and adiabatic  $\tilde{A} - \tilde{X}$  energy separation were calculated by the TDDFT and CIS methods, respectively. Table 4 gives the calculated energies of the  $G_1G_2$  and  $G_1G'_2$ conformers in  $\tilde{X},\,\tilde{A}$  and  $\tilde{B}$  electronic states. The disagreement between the experimental and the theoretical values is especially large, but this calculation result also supports the 2cyclohexlethoxy lies the closely energy between X and A electronic states.

According to the experimental spectrum and the assignment above, we can conclude that for both of the  $G_1G_2$  and  $G_1G'_2$ conformers the LIF spectrum abruptly terminates at  $\leq 600 \text{ cm}^{-1}$ above its origin with only one quantum of C-O stretch observed. This is in remarkable contrast to the previous reported spectra of methoxy, ethoxy, 2-propoxy and t-butoxy.<sup>4,6,30</sup> In each of these cases, the excitation spectra contained at least 5 quanta of C-O stretch excitation and extend for  $\geq 30\ 000\ \text{cm}^{-1}$  above the origin. This may because the methoxy, ethoxy, 2-propoxy and tbutoxy have only one conformer, while there is more than one conformer for 2-cyclohexlethoxy due to the ring structure. In the case of 2-cyclohexlethoxy, which have multiple conformers, the abrupt termination of the spectrum was attributed to rapid internal conversion to the X state that occurs upon vibrational excitation, an explanation that likely accounts for the similar behavior in 1-propoxy. There are two other possible nonradiative paths that 2-cyclohexlethoxy can occur C-C bond fission and nonclassical C-H···O hydrogen bonding of the O atom to one of  $\gamma$  or  $\delta$  H which are possible in  $G_1G_2$ ,  $G_1G'_2$  and T<sub>1</sub>G<sub>2</sub> conformers. As the calculation results are showed in Table 1, the barriers of C-C bond fission of the three conformers are closely 13.6 kcal mol<sup>-1</sup> with the little discrepancy 0.2 kcal mol<sup>-1</sup>. The G<sub>1</sub>G<sub>2</sub> conformer is easy to obtain C–C bond fission that is 2.0 kcal  $mol^{-1}$  lower in energy than that for isomerization via a 1, 4 H-shift. However, the  $G_1G'_2$  isomerization in a 1, 5

H-shift is favor to consider, because the barrier is 3.8 kcal mol<sup>-1</sup> lower than that for C–C bond fission. In our LIF experiment, photolysis of the primary cyclohexylmethyl and 2-cyclohexyethyl nitrites both acquired corresponding 1-alkoxy that undergone decomposition to produce formaldehyde. The energy of band K frequency or a higher frequency in excitation laser is at least 4.0 kcal mol<sup>-1</sup> higher than that for photolysis laser. Therefore, we can sure formaldehyde will inevitably be produced in scanning excitation wavelength above band K frequency for 1-alkoxy. According to our LIF spectrum and calculation results, the assigning  $G_1G_2$  and  $G_1G'_2$  conformers undergone isomerization or decomposition with a compete reactive, which will lead to nonradiative mechanism of 1-alkoxy on the  $\tilde{B}$  excited state that no  $\nu' > 1$  C–O stretch was observed in the jet-cooled spectrum.

2-Cyclohexlethoxy was generated by replacing the H atom on β carbon of ethoxy with cyclohexyl, while a methyl substituted became 1-propoxy. If we use the origin (29 210 cm<sup>-1</sup>) of ethoxy as a reference, then the origins of T and G 1-propoxy are shifted by +9 cm<sup>-1</sup> and -576 cm<sup>-1</sup>. The implication would be that adding an additional  $CH_2$  to ethoxy shifts the  $\tilde{X}$  and  $\tilde{B}$  states almost exactly equally so long as  $C_s$  symmetry is maintained. However by rotating the O out-of-plane in the G conformer the B state is stabilized with respect to the T conformer by nearly  $600 \text{ cm}^{-1}$ . The  $G_1G_2$  and  $G_1G'_2$  of 2-cyclohexlethoxy in which the oxygen atom is rotated out of plane are both  $C_1$  symmetry, then the origin of both conformers in our assignment are shifted by -280 cm<sup>-1</sup> and -165 cm<sup>-1</sup> compared to the origin of ethoxy. Our computations using the CASSCF (9,7) method for the  $\tilde{B}$  state, are consistent with spectrum assignment that the origin of G1G2 is about 100  $\text{cm}^{-1}$  below the  $G_1G'_2$  conformer. If we consider conformer  $G_1G'_2$  as a reference, then this implies that the  $\tilde{B}$  state of  $G_1G_2$  conformer is stabilized by  $\geq 100$  cm<sup>-1</sup>. We can rationalize this observation as follows. In the case of conformer G1G2 and  $G_1G'_2$ , the stabilization compared to the origin of ethoxy may be attributed to a nonclassical C-H···O hydrogen bond, which is more important in the B state because of the larger volume of the doubly occupied p-orbitals on the oxygen atom. A similar observation was made in the analogous gauche conformer of 1-propoxy. It is another probable that  $G_1G_2$  conformer relative to  $G_1G_2$ of 2-cyclohexlethoxy is destabilized because of steric repulsion between the O atom and  $\delta$  H atom.

### 5 Conclusions

In this work, we report the LIF excitation spectrum following photolysis of cyclohexylmethyl and 2-cyclohexylethyl nitrites.

The only rotationally resolved formaldehyde line appears in the narrow wavelength region of 28 290 to 28 350 cm<sup>-1</sup> in the photolysis precursor cyclohexylmethyl nitrites. However, a weaker formaldehyde line and a resolved vibrational 2-cyclohexylethoxy spectrum were acquired in the photolysis precursor 2-cyclohexylethyl nitrites. As for our experiment and calculation result, the big cyclohexyl group substituent the  $\alpha$  H of CH<sub>3</sub>O suggested to be the cause of the reduced barrier to decomposition compare to  $\beta$  H of CH<sub>3</sub>CH<sub>2</sub>O. It is probable that an increasing steric repulsion and few conformers for cyclohexylethoxy relative to 2-cyclohexylethoxy will difficult internal conversion to the  $\tilde{X}$  state and lead to enough energy to unimolecularly dissociate to C<sub>6</sub>H<sub>11</sub> + H<sub>2</sub>CO.

For the first time, a nicely resolved vibrational structure LIF spectrum of 2-cyclohexylethoxy was acquired in the wavelength region of 28 800 to 29 800 cm<sup>-1</sup>. This spectrum was assigned preliminarily to G1G2 and G1G2 conformers of 2-cyclohexylethoxy. Compared to the previous work of 1-ethoxy and 1propoxy, the LIF spectrum of 1-ethoxy has been observed a long C-O stretch progressions, while spectrum of 1-propoxy is similar behavior to 2-cyclohexylethoxy that no  $\nu > 1$  C–O stretch was observed in the jet-cooled spectrum. By a combination of experimental electronic origins and computational results, we can learn a considerable amount about subtle stabilization effects depending on molecular geometry. In each conformer the highest energy vibrational band observed corresponds to one quanta of C-O stretch excitation. It is speculated that the quantum yield for emission from higher vibrational levels falls dramatically due to internal conversion between cyclohexyl and C-C backbone. Furthermore, dissociation in C-C bond fission and isomerization induced by H transfer via a ring configuration might also play an important role in the relaxation process of 2-cyclohexylethoxy on the  $\beta$  excited state. However, further experimental and theoretical studies are required to fully understand the relaxation mechanism of the ß excited state and verify the spectral assignment of 2-cyclohexylethoxy radicals.

## Acknowledgements

The authors are pleased to acknowledge the financial support of this startup project for high-level talents of Guizhou Institute of Technology (XJGC20150101). We also acknowledge the financial support of this research by the Natural Science Research Project of Guizhou Provincial Education Office in 2013 ([2013]180 and [2013]181) and support from Guizhou Province Science and Technology Fund in 2013 ([2013]2006 and [2013]2007). The authors gratefully acknowledge helpful discussions with Professor Lily Zu of Beijing Normal University.

## References

- 1 J. John, L. T. Iraci and G. S. Tyndall, *J. Phys. Chem. A*, 2000, **104**, 5072–5079.
- 2 J. Lin, L. Zu and W. Fang, J. Phys. Chem. A, 2011, 115, 274-279.
- 3 S. M. Aschmann, A. A. Chew, J. Arey and R. Atkinson, *J. Phys. Chem. A*, 1997, **101**, 8042–8048.

- 4 D. E. Powers, M. B. Pushkarsky and T. A. Miller, *J. Chem. Phys.*, 1997, **106**, 6863–6877.
- 5 J. Liu, M. W. Chen, D. Melnik, T. Y. John and T. A. Miller, *J. Chem. Phys.*, 2009, **130**, 074302.
- 6 X. Q. Tan, J. M. Williamson, S. C. Foster and T. A. Miller, *J. Phys. Chem.*, 1993, **97**, 9311–9316.
- 7 C. C. Carter, S. Gopalakrishnan, J. R. Atwell and T. A. Miller, *J. Phys. Chem. A*, 2001, **105**, 2925–2928.
- 8 S. Gopalakrishnan, C. C. Carter, L. Zu, V. Stakhursky, G. r. Tarczay and T. A. Miller, *J. Chem. Phys.*, 2003, **118**, 4954–4969.
- 9 S. Gopalakrishnan, L. Zu and T. A. Miller, *J. Phys. Chem. A*, 2003, **107**, 5189–5201.
- 10 L. Zu, J. Liu, S. Gopalakrishnan and T. A. Miller, *Can. J. Chem.*, 2004, **82**, 854–866.
- 11 L. Zu, J. Liu, G. r. Tarczay, P. Dupré and T. A. Miller, *J. Chem. Phys.*, 2004, **120**, 10579–10593.
- 12 D. Nasipuri, *Stereochemistry in Organic Compounds, Principles and Applications*, New Age International (P) Ltd. Press, New Delhi, 1994.
- 13 Q. Wu, G. Liang, L. Zu and W. Fang, J. Phys. Chem. A, 2012, 116, 3156–3162.
- 14 A. H. Blatt, Organic Syntheses, Wiley, New YorK, 1966.
- 15 M. Rosenberg and T. I. Sølling, *Chem. Phys. Lett.*, 2010, **484**, 113–118.
- 16 W. Henke, H. Selzle, T. Hays, E. Schlag and S. H. Lin, *J. Chem. Phys.*, 1982, **76**, 1327–1334.
- 17 R. J. Bouwens, J. A. Hammerschmidt, M. M. Grzeskowiak, T. A. Stegink, P. M. Yorba and W. F. Polik, *J. Chem. Phys.*, 1996, **104**, 460–479.
- 18 A. Burkert, D. Grebner, D. Müller, W. Triebel and J. König, *Proc. Combust. Inst.*, 2000, 28, 1655–1661.
- 19 R. Bombach and B. Käppeli, Appl. Phys. B, 1999, 68, 251-255.
- 20 E. L. Eliel, S. H. Wilen and L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley Press, New York, 1997.
- 21 J. Lin, Q. Wu, G. Liang, L. Zu and W. Fang, *RSC Adv.*, 2011, 2, 583–589.
- 22 T. A. Miller, Mol. Phys., 2006, 104, 2581-2593.
- 23 G. Tarczay, S. Gopalakrishnan and T. A. Miller, *J. Mol. Spectrosc.*, 2003, **220**, 276–290.
- 24 D. L. Osborn, D. J. Leahy and D. M. Neumark, *J. Phys. Chem. A*, 1997, **101**, 6583–6592.
- 25 L. Lin, L. L. Zu, W. H. Fang, J. G. Yu and R. Z. Liu, *Chin. J. Chem.*, 2007, **25**, 1467–1473.
- 26 X. Zhu, M. M. Kamal and P. Misra, *Pure Appl. Opt.*, 1996, 5, 1021–1029.
- 27 J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc., Pittsburgh, PA, 1996.
- 28 J. Jin, I. Sioutis, G. r. Tarczay, S. Gopalakrishnan, A. Bezant and T. A. Miller, *J. Chem. Phys.*, 2004, **121**, 11780–11797.
- 29 R. Chhantyal-Pun, M. Roudjane, D. G. Melnik, T. A. Miller and J. Liu, *J. Phys. Chem. A*, 2014, **118**, 11852–11870.
- 30 C. C. Carter, J. R. Atwell, S. Gopalakrishnan and T. A. Miller, *J. Phys. Chem. A*, 2000, **104**, 9165–9170.