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Research paper

The high-resolution infrared spectrum of the $\nu_3 + \nu_5$ combination band of jet-cooled propyne

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ABSTRACT

We present the first detection of the high-resolution ro-vibrational spectrum of the $\nu_3 + \nu_5$ combination band of propyne around 3070 cm^{-1}. The fully resolved spectrum is recorded for supersonically jet-cooled propyne using continuous wave cavity ring-down spectroscopy (cw-CRDS). The assignments are supported with the help of accurate *ab initio* vibration-rotation interaction constants (α_i) and anharmonic frequencies. A detailed analysis of the rotationally cold spectrum is given.

1. Introduction

Propyne, also known as methylacetylene ($H_3C{-}C{\equiv}CH$), is a small unsaturated hydrocarbon of astrophysical importance. It is believed to play a role in the chemistry of a number of hydrocarbon-rich astronomical objects, including the atmosphere of Titan [1], the dark cloud TMC-1 [2], the circumstellar shell of the AGB star IRC+10216 [3], and two protoplanetary nebulae CRL 618 [4] and SMP LMC 11 [5], where it has been observed in the infrared (IR) through the ν_9 (H—C≡C bending) mode, and by radio astronomy through pure rotational transitions. In addition, the close spacing of the rotational transitions of different K' subbands, and the relatively low dipole moment ($\mu = 0.78$ D) [6] make propyne an ideal probe of the interstellar medium's kinetic temperature; since the excitation temperature increases as K' increases [7–9].

From a pure spectroscopic point of view this molecule is also interesting. As a prolate symmetric top the aliphatic (CH_3) and acetylenic (CH) stretches are suitably decoupled from each other that the strong acetylenic CH stretch mode (ν_1) is not strongly perturbed [10]. Studies of spectra that are perturbed through weak near-resonant couplings to background vibrational states, as seen in other transitions of propyne, make it of interest for studying intramolecular vibrational relaxation (IVR) [11–13,10,14–17]. Moreover, comparison between high-resolution measurements as presented here for propyne and *ab initio* methods offers a good test of the accuracy of the Hamiltonians used to describe the involved molecular energy levels.

Propyne has been extensively studied in the electronic ground state (X^1A_1) through a number of microwave and IR experimental studies and *ab initio* calculations (Ref. [18], and references therein). In fact, all of the fundamental bands and a substantial number of combination bands involving either ν_3 (C≡C stretch) or ν_5 (C—C stretch) excitations have been studied at high-resolution [19–23,10,14,16,24,9,18,25,26]. The spectroscopic identification of the $\nu_3 + \nu_5$ combination band has not yet been reported. Based on the published band origins for ν_3 [20] and ν_5 [25], the $\nu_3 + \nu_5$ combination band is expected at ~ 3068 cm^{-1}.

The results of a survey around this wavelength are presented here. The experimental and theoretical details are given in Section 2. The spectroscopic analysis and discussion are presented in Section 3. Line positions are available from the supplementary material.

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2. Methods

2.1. Experimental

The experimental setup has been described in detail in Ref. [27], and has recently been used to measure the $\nu_3 + \nu_8$ combination band, involving the CH_3 rocking mode of jet-cooled propyne around 3175 cm^{-1} [26]. The main difference with the present experiment is that a different single-mode continuous-wave optical parametric oscillator (cw-OPO) had to be used; the Aculight, Argos 2400-SF-C module that covers 3.2–3.9 µm is used, instead of the B module, which covers 2.5–3.2 µm.

A gas mixture of 0.05% propyne in 1:1 argon:helium is used as the precursor gas. The gas is then supersonically expanded with a 4 bar backing pressure through a long (0.3×30 mm) slit nozzle connected to a pulsed valve (General valve, serial 9) [28] into a vacuum chamber with a stagnation pressure of $\sim 1.5 \times 10^{-2}$ mbar, realized by a large roots blower system with a total pumping capacity of 4800 m^3/hr. The valve runs at 10 Hz, and the typical gas pulse has a duration of about 800 µs. The pulsed gas flow is used to create a high pressure jet expansion, increasing the local number density of propyne molecules at the nozzle slit.

The absorption spectrum is recorded using cw-CRDS, with the IR laser path intersecting the expansion roughly 1 cm downstream from the nozzle body. The optical cavity is comprised of two highly reflective plano-concave mirrors ($R \sim 99.98\%$, centered at 3300 cm^{-1}). Typical empty cavity ring-down times (τ_0) are about 9 µs. The hardware (boxcar integrator) based multi-trigger and timing scheme described in detail in Ref. [27] is used to coincide the laser light and gas pulse. This guarantees that the trigger scheme compensates for the low duty cycle when combining a cw laser with a pulsed gas expansion. For this experiment the optical cavity length is modulated at ~ 26 Hz, using a piezo crystal mounted on the back of one of the cavity mirrors.

The resulting spectrum is recorded in a series of ~1.2 cm^{-1} parts that partially overlap to guarantee that spectra can be directly compared. While the spectrum is recorded, the laser frequency is simultaneously measured using a wavelength meter (Bristol Instruments, 621A-IR). The frequency accuracy is independently calibrated by measuring known transitions of ethylene (C_2H_4) [29]. The resulting maximum frequency uncertainty of ± 0.002 cm^{-1} is dictated by the wavemeter.

2.2. Theoretical

Equilibrium geometry and second-order vibrational perturbation theory (VPT2) calculations are carried out at the CCSD(T) level of theory. The core-valence correlation-consistent quadruple-ζ basis set (cc-pCVQZ) [30] is used to determine the equilibrium geometry and rotational constants, since it has been shown to give highly accurate geometries for acetylenic molecules [31,32]. The atomic natural orbital (ANO) basis set with the truncation [4s3p2d1f] for non-hydrogen atoms and [4s2p1d] for hydrogen (hereafter known as ANO1) [33] is used to determine the anharmonic vibrational frequencies and electronic ground state spectroscopic constants of propyne. It has been shown to reproduce experimental frequencies better than the correlation-consistent basis sets [34,32]. All calculations are performed with the development version of the CFOUR program [35].

3. Results and discussion

An overview of the experimental spectrum is shown in the upper trace of Fig. 1(a). It shows a regular pattern with excellent signal-to-noise spreading over 15 cm^{-1}. A parallel band consistent with a C_{3v} symmetric top molecule A_1-A_1 transition is clearly seen with a Q-branch at ~3070.1 cm^{-1}, very close to the predicted $v_3 + v_5$ frequency of 3068 cm^{-1}. The experimental spectrum is analyzed using the PGOPHER software [36], assuming a rotational temperature of 18 K and a Gaussian linewidth of 0.004 cm^{-1}. The latter is determined by minimal residual Doppler broadening in the slit nozzle expansion. A first fit of the strongest transitions gives lower state rotational constants in good agreement with

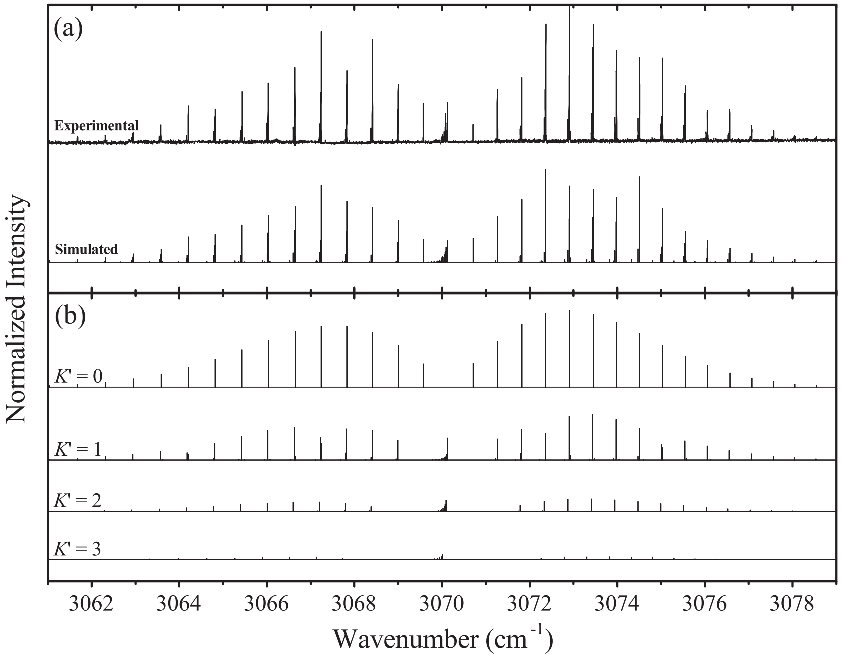

Fig. 1. (a) The experimental spectrum from 3059.5 to 3080.5 cm^{-1} (upper trace), and simulated spectrum (lower trace) of the $\nu_3 + \nu_5$ combination band comprising of different K' subbands. (b) Simulations of the K' = 0, 1, 2, and 3 subbands (including transitions to perturbing states). A rotational temperature of 18 K is used in the simulated spectra.

Table 1
Spectroscopic parameters of the vibrational levels ν_3, ν_5, and $\nu_3 + \nu_5$ state[a] (in cm^{-1}).

	Ground state[b]	ν_3	ν_5	$\nu_3 + \nu_5$			
	[25]	[20]	[25]	$K = 0$	$K = 1$	$K = 2$	$K = 3$
E	0.0	2137.87(12)	930.276 530(21)	3070.1411(4)	3070.1411[b]	3070.1411[b]	3070.1411[b]
A	5.308 312 9	5.301 7(2)	5.300 964 6(26)	–	5.293 07(40)	5.294 17(12)	5.294 91(10)
$\alpha_i^A \times 10^3$		6.613	7.348				
B	0.285 059 768 3	0.283 550(2)	0.283 800 493(11)	0.282 428(8)	0.282 432(9)	0.282 508(17)	0.282 323(223)
$\alpha_i^B \times 10^3$		1.510	1.259				
$D_J \times 10^7$	0.980 422	0.975(5)	1.024 005(80)	0.857(350)	0.769(371)	5.99(96)	$3.99(41) \times 10^2$
$D_{JK} \times 10^5$	0.545 095 8	0.513(2)	0.563 033 4(239)				
$D_K \times 10^5$	9.701 5		9.696 5(74)				
$H_J \times 10^{15}$	−2.227		263.97(189)				
$H_{JK} \times 10^{11}$	3.050 3		1.781 5(66)				
$H_{KJ} \times 10^{10}$	1.769 1		−7.504 6(237)				
$H_K \times 10^8$	0.0		−0.270 0(539)				
$L_{JJK} \times 10^{15}$	−0.210 5		0.0				
$L_{JK} \times 10^{15}$	−1.451		0.0				
$L_{KKJ} \times 10^{15}$	−13.55		0.0				

[a] Numbers in parenthesis are one standard deviation in units of the last significant digit.
[b] Fixed values.

those already known for propyne. For a more accurate rotational analysis the lower state constants are fixed to the ground state parameters reported by Pracna et al. [25]. The rotational constants for the upper state are calculated by the standard relation for a prolate symmetric top molecule:

$$E(\mathrm{v_i}, J, K, l) = E(\mathrm{v_i}) + 2A\zeta lK + (A - B)K^2 + BJ(J + 1) - D_J J^2(J + 1)^2 - D_{JK}J(J + 1)K^2 - D_K K^4 \quad (1)$$

where D_J, D_{JK}, and D_K are the centrifugal distortion constants, ζ is the coriolis coupling constant (in this case $\zeta = 0$), l is the quantum number related to the projection of the total vibrational angular momentum on the symmetry axis, and A and B are the rotational constants, which can be given as:

$$A_v = A_0 - \Sigma(\mathrm{v_i}\alpha_i^A) \quad (2)$$

$$B_v = B_0 - \Sigma(\mathrm{v_i}\alpha_i^B) \quad (3)$$

where α_i is the vibration-rotation interaction constant.

The rotational analysis starts from a least-squares fit, which gives excited state parameters that reproduce the overall pattern with reasonable accuracy. However, many of the $K' = 1$ and 2 transitions show large deviations between the observed and calculated frequencies, suggestive of perturbations. As such, the K' subbands were fit separately, based on the method described by Zhao et al. [26]; this is shown in Fig. 1b. The resulting effective spectroscopic parameters, and the parameters of the ν_3 [20] and ν_5 [25] states are summarized in Table 1. From a least-squares fit of the $K' = 0$ subband the band origin is determined to be 3070.1411(4) cm^{-1} (which we fix for the $K' > 0$ subbands), and $B' = 0.282428(8)$ cm^{-1}. In addition to transitions to the main state, transitions to three perturbing states are identified in the experimental spectrum, and the spectroscopic parameters of those bands are summarized in Table 2. The o-c (obs.-calc.) values of all the assigned transitions are listed in the Supplementary Material. The summed spectrum of all the individual simulated subbands, including transitions to perturbing states, is given in the lower trace of (a) in Fig. 1, and a zoom-in of the Q-branch is given in Fig. 2. This shows that the measured and simulated spectra are in excellent agreement. As in the jet-cooled propyne study described previously by Zhao et al. [26], only one rotational temperature of 18 ± 2 K, and a 1:1 E: (A_1, A_2) statistical weights is needed to reproduce the overall observed intensity pattern.

Table 2
Effective spectroscopic parameters of the perturbing states[a] (in cm^{-1}).

	$K' = 1$		$K' = 2$
	P1	P2	P3
State symmetry	A_1	A_1	A_1
E	3070.0682(7)	3069.9488(6)	3070.1082(8)
A	5.335 30(126)	5.333 10(592)	5.299 31(42)
B	0.284 210(56)	0.284 160(75)	0.281 290(279)
Perturbation coefficient	0.007(1)	0.011(1)	0.009(1)

[a] Numbers in parenthesis are one standard deviation in units of the last significant digit.

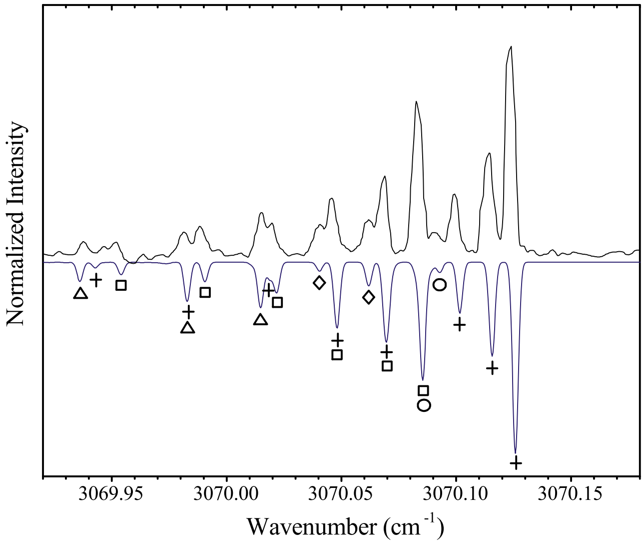

Fig. 2. A zoom-in of the Q-branch region of the experimental (upper trace) and sum simulated (lower trace) spectrum. Transitions of the $\nu_3 + \nu_5$ subbands are labelled: $K' = 1$ with crosses, $K' = 2$ with squares, and $K' = 3$ with triangles, and the perturber bands (designated P_n) are labelled: $K' = 1$ P1 with circles and $K' = 2$ P1 with diamonds; some of the transitions are blended. The transitions are fit using a Gaussian linewidth of 0.004 cm^{-1}.

The 3000 cm^{-1} region of the propyne spectrum is expected to have a high density of states, many of which originate from high-order combination states. As such, the assignment of the experimental data is supported by *ab initio* calculations. The CCSD(T)/ANO1 VPT2 calculations of propyne are able to predict the

Table 3
Harmonic and anharmonic (VPT2) frequencies of propyne[a] (in cm^{-1}).

		CCSD(T)/ANO1		Experimental
	Nuclear motion	Harmonic frequency, ω	VPT2 anharmonic frequency,[a] ν	Fundamental frequency, ν
$\nu_1(A_1)$	CH stretch	3471.5	3338.0(46.6)	3335.065 90 [10]
$\nu_2(A_1)$	CH_3 sym. stretch	3050.3	2938.8(9.5)	2940.999 6 [21]
$\nu_3(A_1)$	C≡C stretch	2180.2	2138.0(3.1)	2137.87 [20]
$\nu_4(A_1)$	CH_3 umbrella motion	1414.3	1382.7(0.0)	1385.03 [19]
$\nu_5(A_1)$	C—C stretch	935.3	924.2(0.5)	930.276 530 [25]
$\nu_6(E)$	CH_3 asym. stretch	3126.4	2976.8(7.3)	2980.860 2 [21]
$\nu_7(E)$	CH_3 scissoring	1486.6	1449.4(7.7)	1450.271 [19]
$\nu_8(E)$	CH_3 rocking	1057.0	1034.3(0.1)	1036.147 539 [25]
$\nu_9(E)$	H—C≡C bending	642.8	635.5(45.6)	638.569 14 [23]
$\nu_{10}(E)$	C—C≡C bending	325.3	327.8(7.6)	330.938 56 [22]
$\nu_5 + \nu_{10}(E)$		1260.6	1254.9(0.02)	1262.75 [19]
$\nu_5 + \nu_9(E)$		1578.1	1558.3(0.002)	1566.18 [19]
$\nu_5 + \nu_8(E)$		1992.4	1956.3(0.002)	1989.7 [20]
$\nu_5 + \nu_8 + 3\nu_{10}(A_1 + A_2)$		2968.2	2940.0(0.0)	2940.833 [21]
$\nu_3 + \nu_5(A_1)$		3115.6	3060.1(0.14)	3070.1411[b]
$\nu_3 + \nu_8(E)$		3237.3	3170.5(0.05)	3176.0774 [26]
$\nu_3 + \nu_6(E)$		5306.6	5114.3(0.01)	5122.0 [18]
$\nu_1 + \nu_3(A_1)$		5651.7	5468.7(0.007)	5465.0 [24]
$\nu_1 + \nu_3 + \nu_5(A_1)$		6587.0	6390.9(0.0)	6398.05 [16]
$2\nu_1(A_1)$		6942.9	6567.2(1.2)	6568.172 [14]
$2\nu_1 + \nu_5(A_1)$		7878.3	7491.5(0.0)	7500.6 [18]
$2\nu_1 + \nu_3(A_1)$		9123.2	8690.6(0.0)	8691.3 [18]
ZPE = 12003.1				

[a] Intensities in km/mol are given in parenthesis.
[b] This work.

anharmonic frequencies and intensities of fundamental and combination states; this applies even to states with ten or more quanta of excitation. However, states involving three or less quanta of excitation are believed to be the most accurate, since many states at that level can be compared to experimentally determined band origins [18]. As shown in Table 3, our VPT2 calculations are able to reproduce the experimental frequencies of both fundamental and combination bands to within 10 cm^{-1}. This suggests that the predicted anharmonic frequencies for new transitions are equally accurate. Within ~100 cm^{-1} of 3070 cm^{-1} the calculations predict only three states with appreciable IR intensity: ν_6 at 2976.8 cm^{-1}, and $\nu_3 + \nu_8$ at 3170.5 cm^{-1}, which are both E states, and $\nu_3 + \nu_5$ at 3060.1 cm^{-1}, which is an A_1 state (Table 3). The calculated anharmonic frequency for $\nu_3 + \nu_5$ at 3060.1 cm^{-1} has an o-c difference of 10.04 cm^{-1} relative to our experimentally determined band origin, which is consistent with that expected for the accuracy of our calculations. In addition, both the calculated and experimental values agree well with the frequency predicted based on the experimental frequencies of the ν_3 and ν_5 fundamental bands (Table 1), strongly supporting the assignment of the new experimental band as the $\nu_3 + \nu_5$ combination band of propyne.

Furthermore, the CCSD(T)/ANO1 calculations result in vibration-rotation interaction constants (Table 4) that are in much better agreement with experimentally derived values compared to previous calculations, particularly α_i^A [10]. From Eqs. (2) and (3), the $\nu_3 + \nu_5$ rotational constants based on our calculated α_i (Table 4) are A = 5.2997 cm^{-1} and B = 0.28500 cm^{-1}, and based on the experimental α_i (Table 1) we find A = 5.2944 cm^{-1} and B = 0.28506 cm^{-1}. Both predicted B_{3+5} values differ by less than 1% from our experimental B′, providing additional support for the assignment of the $\nu_3 + \nu_5$ combination band to the experimentally observed band shown in Fig. 1.

For the fit, 31 transitions are assigned to the $\nu_3 + \nu_5$ state $K' = 0$ subband, while only 3 transitions are assigned to the $K' = 3$ subband. The fitting of the $K' = 0$ and 3 subbands (both A_1-A_2 type transitions) do not show signs of perturbations. However, in the present data set we cannot exclude perturbations in the $K' = 3$ subband, since only a limited number and only Q-branch transitions are observed. We also cannot exclude any perturbations at high-J' K' in any of the subbands. Conversely though, 34 transitions are assigned to the $K' = 1$ subband of the $\nu_3 + \nu_5$ state, and 26 transitions are assigned to the $K' = 2$ subband. The $K' = 1$ and 2 subbands (both E-E type transitions) require the inclusion of perturbing states in the fit in order to accurately reproduce the observed line positions.

Table 4
CCSD(T)/ANO1 vibration-rotation interaction constants of propyne[a] (in cm^{-1}).

Mode	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$
ν_1	0.035*(0.41)* [10]	0.646*(0.665)* [21]
ν_2	55.44*(38)* [37]	0.077*(0.084)* [21]
ν_3	2.570*(6.6)* [20]	1.476*(1.510)* [21]
ν_4	−27.42	1.665*(0.40)* [21]
ν_5	6.012*(7.572)* [6]	1.285*(1.260)* [21]
ν_6	35.87*(17)* [38]	0.064*(0.026)* [21]
ν_7	39.68*(42.89)* [19]	−0.887*(−0.26)* [21]
ν_8	−29.49*(−61.8)* [20]	0.196*(0.141)* [21]
ν_9	0.652*(1.353)* [39]	−0.187*(−0.18)* [21]
ν_{10}	1.293*(2.170)* [22]	−0.821*(−0.78)* [21]

[a] Experimental values are given in parenthesis.

The perturbing states all have the same A_1 symmetry, and we assume that all of the perturbations are homogeneous perturbations that to our best approximation are independent of any quantum numbers. Two perturbing states are required to accurately reproduce the experimental line positions of the $\nu_3 + \nu_5$ state $K' = 1$ subband. One (P1) with a perturbation coefficient of 0.007(1) cm^{-1} has 8 observed transitions, including a noticeable Q-branch, and it affects the $J' \leqslant 5$ transitions. While the second (P2) only has 4 observed transitions, with no observed Q-branch transitions, but it has a larger perturbation coefficient of 0.011(1) cm^{-1} and strongly affects $J' = 9$. Finally, while only 2 transitions are observed to the P3 states, the interaction has a perturbation coefficient of 0.009(1) cm^{-1}, and significantly influences the $J' \leqslant 7$ transitions, particularly the Q-branch, of the $\nu_3 + \nu_5$ $K' = 2$ subband. Unfortunately, at this time we cannot conclusively identify the perturbing states. However, with the inclusion of the perturbing states the least-square fit analysis gives an effective A = 5.293 07(40), 5.294 17(12), and 5.294 91(10) cm^{-1}, for the three K' subbands respectively, which all differ by less than 0.1% from the predicted A_{3+5} values.

The present data set can be compared with the results presented by Zhao et al. [26]. The VPT2 calculations predict the intensity of the $\nu_3 + \nu_5$ combination band to be about 3× the intensity of the $\nu_3 + \nu_8$ combination band. A comparison of the $\nu_3 + \nu_5$ data presented here and the $\nu_3 + \nu_8$ data published earlier by Zhao et al. [26] – all recorded for similar expansion conditions and corrected for small changes in the ring-down time – results in a factor 2.8× difference in the intensity. This provides a further argument supporting the assignment made here.

4. Conclusion

The current high-resolution study of jet-cooled propyne using cw-CRDS has yielded the first fully resolved observation of the $\nu_3 + \nu_5$ state. As also found in the recent work on $\nu_3 + \nu_8$, our analysis indicates that near-resonant or non-resonant perturbations are involved in the $\nu_3 + \nu_5$ spectrum. The experimental data are fully consistent with high level *ab initio* calculations, presented here, for the anharmonic frequencies. These calculations also give ground state spectroscopic constants accurate enough to aid in the assignment of ro-vibrational spectra of propyne.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2017.07.022.

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