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# High-resolution synchrotron infrared spectroscopy of acrolein: The vibrational levels between 850 and 1020 $\text{cm}^{-1}$

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## ABSTRACT

Using spectra obtained at the Canadian Light Source synchrotron radiation facility, a previously unobserved out-of-plane vibration of *trans*-acrolein (propenal) is reliably assigned for the first time. Its origin is at 1002.01  $\text{cm}^{-1}$ , which is about 20  $\text{cm}^{-1}$  higher than usually quoted in the past. This mode is thus labelled as  $\nu_{14}$ , leaving the label  $\nu_{15}$  for the known vibration at 992.66  $\text{cm}^{-1}$ . Weak combination bands  $17^1 18^2 \leftarrow 18^2$ ,  $17^1 13^1 \leftarrow 13^1$ ,  $12^1 18^2 \leftarrow 18^1$ , and  $17^1 18^2 \leftarrow 18^1$  are studied for the first time, and assignments in the known  $\nu_{11}$ ,  $\nu_{16}$ , and  $\nu_{15}$  fundamental bands are also extended. The seven excited vibrations involved in these bands are analyzed, together with five more unobserved vibrations in the same region (850–1020  $\text{cm}^{-1}$ ), in a large 12-state simultaneous fit which accounts for most of the many observed perturbations in the spectra.

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## 1. Introduction

In the past few years, we have been studying the molecule acrolein (propenal,  $\text{CH}_2\text{CHCHO}$ ) in a series of papers [1–5] based on high-resolution far infrared spectra obtained at the Canadian Light Source synchrotron radiation facility. This molecule is significant for astrophysics [6], for combustion chemistry, air pollution, and human respiration [7–9]. It is one of 32 primary Hazardous Air Pollutants listed by the U.S. Environmental Protection Agency [10], and one of six priority mobile source toxics listed [11] by the U.S. Federal Highway Administration. The lowest energy *trans* isomer of acrolein is studied here, and relevant previous studies include microwave [12–14] and medium-resolution infrared [15,16] spectra. As well, a comprehensive new microwave study oriented to astrophysical applications has been reported very recently by Daly et al. [17]. In addition to *trans*-acrolein, there is also a higher energy *cis* isomer known from electronic [18–20] and microwave [21] spectra which has not been observed in gas phase in the infrared.

Previously, we reported analyses of all acrolein vibrational states below 700  $\text{cm}^{-1}$  [3] and of those between 700 and 820  $\text{cm}^{-1}$  [5]. Three further states located above 820  $\text{cm}^{-1}$  ( $\nu_{11}$ ,  $\nu_{16}$ , and  $\nu_{15}$ ) were also the subject of a previous paper [4]. Here,

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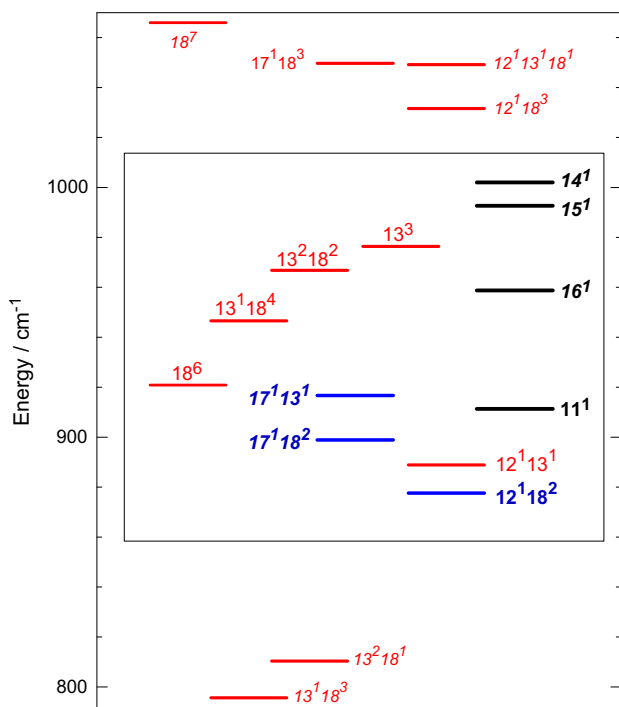
E-mail address: [robert.mckellar@nrc-cnrc.gc.ca](mailto:robert.mckellar@nrc-cnrc.gc.ca) (A.R.W. McKellar).

we refine and extend the latter work by considering all twelve vibrations between 850 and 1020  $\text{cm}^{-1}$ , as shown in a box in Fig. 1. These levels comprise a relatively isolated manifold which (we hope) can be treated in isolation. But of course they are not completely isolated, especially at the upper end (see Fig. 1). For this reason, and because only 8 of the 12 states have been directly observed, our analysis is necessarily incomplete (the other 4 states are ‘indirectly’ observed by means of their perturbations of the observed states). A key result of the present work is the first observation of the weak  $\nu_{14}$  fundamental band at 1002.006  $\text{cm}^{-1}$ . In the past, this out-of-plane vibration was usually reported in the literature to lie around 980  $\text{cm}^{-1}$ , and it was thus usually labelled as  $\nu_{15}$ .

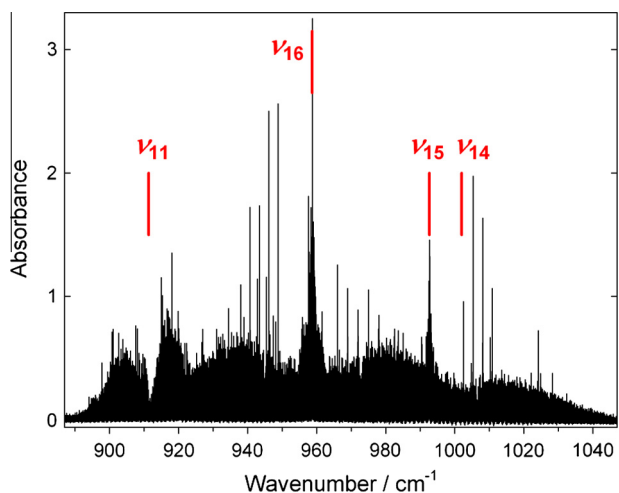
## 2. Results

## 2.1. Experimental details

Spectra were recorded using the Canadian Light Source Bruker IFS 125HR Fourier transform spectrometer, fitted with a KBr beam-splitter and a liquid-helium cooled Ge:Cu detector and operated with the full spectral resolution (0.00064  $\text{cm}^{-1}$  unapodized) given by the 9.4 m maximum optical path difference. Acrolein vapor at pressures of 0.02 or 0.13 Torr was contained in a 2 m multiple-traversal gas cell cooled to about 200 K and set for a total path of 16 or 72 m, respectively. Each spectrum represented a total acquisition time of about 15 h [5].



**Fig. 1.** Vibrational levels of *trans*-acrolein. States of  $A'$  symmetry are labelled in normal script and those of  $A''$  symmetry in italics. The twelve levels in the enclosed box are the subject of the present paper. Observed fundamentals are shown in black, observed combination vibrations in blue, and unobserved or indirectly observed vibrations in red. The labelling of  $14^1$  and  $15^1$  is interchanged compared to previous work. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Overview of the observed spectrum of acrolein in the region of the  $\nu_{11}$ ,  $\nu_{16}$ ,  $\nu_{15}$ , and  $\nu_{14}$  fundamentals (with band origins indicated above). The pressure was 0.02 Torr, the path length was 16 m, and the temperature was 200 K.

We used spectra from three regions: 580–640  $\text{cm}^{-1}$  for the  $17^1 18^2 \leftarrow 18^2$  and  $17^1 13^1 \leftarrow 13^1$  hot bands; 660–760  $\text{cm}^{-1}$  for the  $12^1 18^2 \leftarrow 18^1$  and  $17^1 18^2 \leftarrow 18^1$  hot combination bands; and 850–1050  $\text{cm}^{-1}$  for the  $11^1$ ,  $16^1$ ,  $15^1$ , and  $14^1$  fundamental bands. An overview of the second region (with pressure = 0.13 Torr) is shown in Fig. 2 of Ref. [5], and one of the third region (with pressure = 0.02 Torr) is shown here in Fig. 2.

## 2.2. The acrolein molecule

Acrolein is a planar near-prolate ( $A > B \approx C$ ) asymmetric top molecule with  $C_s$  symmetry. In-plane vibrations ( $\nu_1$ – $\nu_{13}$ ) have  $A'$  symmetry. Out-of-plane vibrations (indicated by italics in Fig. 1) have  $A''$  symmetry. Infrared bands connecting states of the same symmetry have  $a$ - and/or  $b$ -type rotational selection rules, while bands connecting states of different symmetry are  $c$ -type. We used Watson's  $A$ -reduced Hamiltonian [22] and our own multi-state asymmetric rotor fitting program. Unresolved asymmetry doublets were fitted to the mean of their calculated positions. Visualization and peak finding was done using PGOPHER [23]. Ground state rotational parameters were fixed at the microwave values of Winnewisser et al. [14], while those for the  $18^1$ ,  $18^2$ , and  $13^1$  states were fixed at values from Ref. [3]. We also tried the new parameters of Ref. [17], but found that the resulting fit was slightly worse, especially for transitions with high  $K_a$ -values.

Notation for Coriolis- and Fermi-type vibrationally off-diagonal parameters is unfortunately not standardized (see [24–26] for recent examples). For consistency, we continue with the scheme from our previous acrolein work [3,5]:

$$\langle X, k | H | Y, k \rangle = W(X, Y)$$

$$\langle X, k | H | Y, k \pm 1 \rangle = 1/2[\pm G_c(X, Y) + Z_3(X, Z)(2k \pm 1)] \times [J(J+1) - k(k \pm 1)]^{1/2}$$

$$\langle X, k | H | Y, k \pm 2 \rangle = 1/2Z_1(X, Y)\{[J(J+1) - k(k \pm 1)] \times [J(J+1) - (k \pm 1)(k \pm 2)]\}^{1/2}$$

$$\langle X, k | H | Z, k \rangle = [G_a(X, Z) + Z_5(X, Z)J(J+1)]k$$

$$\langle X, k | H | Z, k \pm 1 \rangle = 1/2[G_b(X, Z) \pm Z_3(X, Z)(2k \pm 1)] \times [J(J+1) - k(k \pm 1)]^{1/2}$$

$$\langle X, k | H | Z, k \pm 2 \rangle = \pm 1/2Z_1(X, Z)\{[J(J+1) - k(k \pm 1)] \times [J(J+1) - (k \pm 1)(k \pm 2)]\}^{1/2}$$

Here  $X$  and  $Y$  represent vibrations of the same symmetry ( $A'$  or  $A''$ ), while  $X$  and  $Z$  represent vibrations of different symmetry.  $W$  is the Fermi-type interaction parameter,  $G_a$ ,  $G_b$ , and  $G_c$  are Coriolis parameters, and the  $Z$  are higher order parameters. When Fermi interaction parameters were varied, the *perturbed* band origins (actual positions of the  $J_{KaKc} = 0_{00}$  levels) were used since these tend to be better determined and less correlated [27] than the deperturbed origins.

## 2.3. The $12^1 18^2$ , $12^1 13^1$ , $17^1 18^2$ , and $17^1 13^1$ states

These four states located near 900  $\text{cm}^{-1}$  represent combinations of the  $12^1$  ( $\approx 564 \text{ cm}^{-1}$ ) or  $17^1$  ( $\approx 593 \text{ cm}^{-1}$ ) fundamentals with  $18^2$  ( $\approx 313 \text{ cm}^{-1}$ ) or  $13^1$  ( $\approx 324 \text{ cm}^{-1}$ ). We know that  $18^2$  and  $13^1$  are linked by a fairly substantial (2.65  $\text{cm}^{-1}$ ) anharmonic (Fermi) interaction [3], and expect a similar linking of  $12^1 18^2$  to  $12^1 13^1$  and  $17^1 18^2$  to  $17^1 13^1$ . We also know that  $12^1$  and  $17^1$  are linked by an  $a$ -type Coriolis interaction, and similarly expect analogous effects in the combination states. We discuss these four states together because of their links.

We previously studied the  $12^1 18^1$  and  $17^1 18^1$  combination bands in the 700–750  $\text{cm}^{-1}$  region [5], which are moderately strong, though naturally much weaker than the  $12^1$  and  $17^1$  fundamentals [1,3]. It thus turns out (fortunately!) that the  $12^1 18^2$  and  $17^1 18^2$  states are experimentally accessible by means of the analogous hot combination bands ( $12^1 18^2 \leftarrow 18^1$  and  $17^1 18^2 \leftarrow 18^1$ ) centered at 719.7 and 741.0  $\text{cm}^{-1}$ , respectively. The  $17^1 18^2$  state can also be observed (though not as well) via the doubly hot band  $17^1 18^2 \leftarrow 18^2$  (centered at 585.4  $\text{cm}^{-1}$ ). Similarly, some information on the  $17^1 13^1$  state can be obtained via the  $17^1 13^1 \leftarrow 13^1$  hot band (centered at 592.9  $\text{cm}^{-1}$ ), although transitions with  $K_a' = 2$ –4 were too weak and obscured to assign (see the discussion in Section 4 below). We were not able to directly observe the  $12^1 13^1$  state by means of the  $12^1 13^1 \leftarrow 13^1$  band ( $\approx 565 \text{ cm}^{-1}$ ) or any other band. The reason why  $17^1 13^1 \leftarrow 13^1$  is visible, but not  $12^1 13^1 \leftarrow 13^1$ , is simply that the former is a perpendicular ( $c$ -

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