The $\tilde{A}^{1}Pi_{u}, 0\;1\;1 (\Delta u)$ vibrational level of $\text{C}_3$

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**ABSTRACT**

A new band at $23\;390\;\text{cm}^{-1}$ in the $\tilde{A}^{1}Pi_{u}$--$\tilde{X}^{1}Sigma_{u}^{+}$ electronic transition of $\text{C}_3$ has been recorded by laser-induced fluorescence at high resolution and rotationally analyzed. Based on the agreement of the lower state constants with infra-red data given by Kawaguchi et al. [9], the vibrational assignment is found to be $0\;1\;1 (\Pi_{u})$--$0\;0\;0 (\Sigma_{u}^{+})$. Seventeen of the 19 vibronic levels of the $\tilde{A}^{1}Pi_{u}$ state expected to lie below $25\;700\;\text{cm}^{-1}$ (a vibrational energy of $1025\;\text{cm}^{-1}$) have now been identified.

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1. Introduction

The 405 nm system of $\text{C}_3 (\tilde{A}^{1}Pi_{u}--\tilde{X}^{1}Sigma_{u}^{+})$ is one of the most prominent features in the spectra of comets [1] and has recently been discovered in spectra of the interstellar medium [2,3]. The rotational structure of the system is complicated by perturbations, which have led to some confusion. For instance, the $\tilde{A}^{1}Pi_{u}$--$0\;0\;0$ vibrational level is perturbed at low $J$ values by two “dark” levels, one of which appears to belong to a triplet electronic state [4–7].

In order to observe the $0\;0\;0$--$1\;0\;0$ band (at $23\;451\;\text{cm}^{-1}$) it was necessary to generate “hot” $\text{C}_3$ molecules with an increased population in the ground state $1\;0\;0$ level, which lies at $1224.49\;\text{cm}^{-1}$. This was achieved by photolysis of a mixture of $8$% allene, $52$% argon and $40$% neon, using $193\;\text{nm}$ radiation from an ArF laser. It was found that a gas mixture richer in allene favored higher vibrational temperatures. While scanning the region of the $0\;0\;0$--$1\;0\;0$ band using “hot” $\text{C}_3$ molecules, bands were also found at $23\;384$ and $23\;390\;\text{cm}^{-1}$. The band at $23\;384\;\text{cm}^{-1}$ turned out to be the $1\;2\;1 (~\tilde{A}^{1}Pi_{u})$--$1\;0\;1 (~\tilde{X}^{1}Sigma_{u}^{+})$ band, previously assigned by Baker et al. [8], but the $23\;390\;\text{cm}^{-1}$ band was new. It forms the subject of this article.

2. Results

Fig. 1 illustrates the central part of the $23\;390\;\text{cm}^{-1}$ band, as recorded with the frequency-doubled output of a pulse-amplified Ti:sapphire ring laser. Since this laser system was in a different room from the apparatus recording the $\text{C}_3$ spectrum, the light from it had to be carried by a $50$ m long optical fiber, which has resulted in the rolling baseline and the spectral broadening of the figure. Rotational analysis shows that lines with both odd and even $J$ values are present in all three branches. Since half the lines are missing in a band of $\text{C}_3$, because of the zero nuclear spins of the equivalent carbon atoms, this implies that neither the upper nor the lower state is a $\Sigma$ vibronic level. The first lines of the branches in fact show that the band is of $\Delta$--$\Pi$ type. The line assignments are given in Table 1, along with the derived rotational constants.

The lower state vibrational assignment follows from the $B$ values of the $l$-type doubling components, which are found to be $0.4539\;\text{cm}^{-1}$ (odd $J$) and $0.4456\;\text{cm}^{-1}$ (even $J$). Since the odd $J$ levels have the higher $B$ value, which is the opposite of what is found in the $0\;1\;0 (\Pi_{g})$ level, the lower state must be a $\Pi_{u}$ level, not a $\Pi_{g}$ level. A good match was then found with the infra-red data of Kawaguchi et al. [9] for the $0\;1\;1 (\Pi_{g})$ level, where the $B$ values of the $l$-type doubling components are given as $0.4540$ and $0.4458\;\text{cm}^{-1}$, respectively.

The upper state must then be a $\Delta u$ level. Its energy, $25468.23\;\text{cm}^{-1}$, is given by the sum of the band origins of the $\Delta u$--$0\;1\;1 (\Pi_{g})$ band (from Table 1), the $0\;1\;1 (\Pi_{g})$--$0\;0\;0 (\Sigma_{u}^{+})$ band, from Ref. [9] and the $0\;1\;0 (\Pi_{g})$--$0\;0\;0 (\Sigma_{u}^{+})$ band, from Ref. [10]. This energy corresponds to a vibrational energy of $792.6\;\text{cm}^{-1}$ in
the upper electronic state. The vibrational level must have an odd number of quanta of \( m_3 \), in order for the \( D \) upper state to have \( u \) symmetry, rather than \( g \) symmetry as in the \( \tilde{A} \), 0 1 0 level. Since the \( m_0 = 0 \) fundamental (at 541.7 cm\(^{-1}\)) is the only level of the 00\( v_3 \) manifold with \( v_3 = \text{odd} \) lying below 792.6 cm\(^{-1}\), \([11,12]\) the upper state must have \( v_3 = 1 \) together with 250.9 cm\(^{-1}\) of additional vibrational energy. Given that the 0 1 0 (\( \Delta \)) level of the \( \tilde{A} \) state lies 259.0 cm\(^{-1}\) above the 0 0 0 (\( \Pi \)) level, the assignment of the new level can only be 0 1 1 (\( D \)).

The only rotational perturbation that has been found in the band affects the Q(11) line, which has been displaced to higher frequency by 0.11 cm\(^{-1}\). The perturbing state is not a level of the \( \tilde{A} \Pi_u \) state because the nearest level of that state, 0 4 0 (\( \Pi_u \)), lies 25 cm\(^{-1}\) below, which is too far away for it to be a possible perturber.

With the 0 1 1 (\( \Delta_u \)) level assigned, 17 of the 19 excited vibronic levels of the \( \tilde{A} \Pi_u \) state expected below 25 700 cm\(^{-1}\) (a vibrational energy of 1025 cm\(^{-1}\)) have now been found \([4,11–13]\). The highly irregular course of these levels, which results from the orbital angular momentum of the \( \tilde{A} \Pi_u \) state, is illustrated by the energy level diagram of Fig. 2. The levels that have yet to be found are 0 4 0 (\( \Pi_u \)) and 0 1 1 (\( R \)). They are marked with dashed lines in the figure, and rough estimated positions for them are given in parentheses.

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Fig. 2. The vibrational levels of the $^{1}Π_u$ state of C$_4$ lying below 25 700 cm$^{-1}$. Full lines indicate observed levels, from this work and Refs. [4,11–13]; dashed lines indicate predicted levels that have not been observed so far. The levels are grouped according to their vibrational quantum numbers, shown at the top of the figure.

References