Infrared laser spectroscopy of jet-cooled carbon clusters

Structure of triplet C_6


Department of Chemistry, University of California, Berkeley, CA 94720, USA

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We report the first structural characterization of the triplet isomer of C_6. Forty-one rovibrational/fine structure transitions in the \( \nu_4(\sigma_u) \) antisymmetric stretch fundamental of the C_6 cluster have been measured by diode laser absorption spectroscopy of a supersonic carbon cluster beam. The observed spectrum is characteristic of a centrosymmetric linear triplet state with cumulene-type bonding. The measured ground state rotational constant \( B_0 = 0.048479 (10) \) cm\(^{-1} \) and the effective bond length \( r_{\text{eff}} = 1.2868 (1) \) Å are in good agreement with \textit{ab initio} predictions for the linear triplet \( (^3\Sigma_g^+) \) state of C_6.

1. Introduction

The subject of structure and bonding in small carbon clusters has been of interest to chemists for many years [1]. Recent experiments [2–18] as well as high level \textit{ab initio} calculations [19–30] have largely vindicated the description originally put forth by Pitzer and Clementi [31] in 1959. Clusters with odd numbers of carbons possess linear singlet ground states, whereas even numbered clusters have two low-lying isomers, a triplet linear form and a singlet cyclic form. The bonding in the linear clusters is cumulenic, rather than polyacetylenic. The degree of rigidity in the linear odd numbered clusters has been shown [11] to alternate with the symmetry of the highest occupied molecular orbital (HOMO), such that C_3 and C_7 have filled \( \pi_u \) HOMO's and are the least rigid, while C_5 and C_9 have filled \( \pi_g \) HOMO's and are the most rigid. While the odd numbered clusters C_3, C_5, C_7, and C_9 have been studied in substantial detail, the even numbered clusters have been more elusive. Only the triplet form of C_4 has been characterized in the gas phase [13]. That work indicated the structure of C_4 to be linear, whereas a slightly bent geometry had been observed in rare gas matrices by electron spin resonance (ESR) [17, 18]. No definitive study has been published for the postulated ring structures.

The C_6 cluster has recently been addressed by both theory and experiment. While the early \textit{ab initio} calculations of Raghavachari et al. [23] and Raghavachari and Binkley [24] suggested a singlet cyclic structure to be the ground state, the recent and apparently more sophisticated calculations of Parasuk and Almlöf [27] concluded that a triplet \( (^3\Sigma_g^-) \) linear form with cumulene-type bonding is more stable than singlet cyclic forms. The only experimental results on C_6 available to date are from ESR and infrared absorption experiments in rare gas matrices. Van Zee et al. [15, 16] detected \( \Sigma \) molecules in rare gas matrices by ESR and assigned them to linear C_6, C_8 and C_10 clusters with cumulenic bonding. Recently, the assignments of the matrix
infrared absorption bands, originally proposed by Thompson et al. [32], were reexamined on both experimental [33] and theoretical [28] grounds, and the 1952 cm\(^{-1}\) band was attributed to the linear triplet form of C\(_6\).

2. Experimental

The diode laser spectrometer and the supersonic carbon cluster source used in the present study have been described in detail previously [11] and only a brief description will be given here. Carbon clusters are generated by KrF excimer laser vaporization (200 mJ per pulse at 70 Hz focused to a 0.5 x 15 mm line) of a rotating, translating graphite rod placed in the throat of a pulsed, planar Ar jet (15 atm backing pressure). Absorption spectra of carbon clusters are measured by intersecting the supersonic carbon cluster beam with 20 passes of a focused infrared diode laser beam and monitoring the diode laser power with an InSb detector. The diode laser is stepped in intervals of about 20 MHz every 30–40 excimer laser shots. Absolute and relative frequency calibrations were performed by simultaneously recording the absorption spectrum of allene and the fringe spectrum of a temperature-stabilized air-spaced germanium etalon while monitoring absorption spectra of the carbon clusters. The absorption frequencies of allene in the literature [34] were found to involve large systematic errors, thus they are calibrated here with respect to the absorption lines of H\(_2\)O and CO. The signal to noise ratio achieved with the present apparatus is a factor of 5–10 times better than our previous studies on other carbon clusters. This improvement is based mainly on modification of the gas channel geometry in the cluster source between the pulsed valve and the graphite rod, and careful selection of experimental conditions, especially the alignment and the photon flux condition of the vaporization laser. We will describe details of this improvement in a future paper.

![Typical experimental data and calculated stick spectrum of the \(\nu_4(\sigma_u)\) antisymmetric stretch fundamental of linear triplet \(\left(^3\Sigma_g^+\right)\) C\(_6\). The triplet fine structure was resolved for P(5) through R(7). The calculated spectrum is from the least-squares fit of the observed frequencies and the estimated rotational temperature of 20 K. The transitions shown on the upper part are with \(\Delta J = \Delta N\). The lines with asterisks are currently unassigned.](image)
### Table 1. Observed transitions of the $\nu_4(\sigma_a)$ fundamental of $\text{C}_6 \,^a$

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* Frequencies in parentheses are calculated values for weak undetected transitions whose calculated intensities are near our detection limit. \(\Delta J = \Delta N\) for all the transitions except for those with superscripts \(b (\Delta J = -\Delta N)\) and \(c (\Delta J = 0)\). The calculated frequencies are from a weighted least-squares fit to a model (table 2). The standard deviation of the fit was 0.00072 cm\(^{-1}\).

3. Results and analysis

Guided by the recent reassignment [28, 33] of the Ar matrix absorption band for \(\text{C}_6\), the region from 1957 cm\(^{-1}\) to 1964 cm\(^{-1}\) was searched and about 120 absorption lines were observed. Among these, 41 lines with strongest intensities were found to be assignable to a single vibrational band of a linear triplet carbon cluster. The observed frequencies and assignments of these lines are listed in table 1. Typical data and a calculated stick spectrum are shown in figure 1. The listed transitions were assigned to the \(\nu_4(\sigma_u)\) antisymmetric stretch fundamental of the linear triplet \(\left(^3\Sigma_u^-\right)\) state of \(\text{C}_6\) based on the following criteria: (i) the transitions were observed only from odd \(N\) levels, in agreement with the expected nuclear-spin statistics, (ii) the triplet fine structure splittings observed for \(P(5)\) through \(R(7)\) are the characteristic of the predicted linear triplet state, (iii) the measured rotational constant is in excellent agreement with \textit{ab initio} calculations, and (iv) the observed band origin is in good agreement with \textit{ab initio} predictions, with almost exactly the same relative error as found in analogous predictions for the linear triplet \(\text{C}_4\) cluster [13, 28, 29].

The experimental data were analysed using the following Hamiltonian for both the ground and excited vibrational states [35, 36]:

\[
H_{\text{tot}} = B_v N^2 - D_v N^4 + \frac{2}{3} \lambda_v (3S_z^2 - S^2) + \gamma_v N \cdot S.
\]

Here the first two terms account for the rotational energy, the third term for the...
Table 2. Molecular parameters for the $\nu_4(\sigma_u)$ fundamental in the $^3\Sigma_g^-$ state of C$_6$.
Uncertainties in parentheses are 1σ.

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<th>Rare gas matrix</th>
<th>$Ab\ initio$ theory</th>
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<td>1952-0$^b$</td>
<td>2009$^c$, 2190$^d$, 2179$^e$, 2184$^f$, 1942$^g$</td>
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<td>0-048 04$^c$, 0-049 1$^h$, 0-049 31$^e$, 0-049 4$^j$, 0-047 57$^i$, 0-048 9$^i$</td>
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<td>$D''$/cm$^{-1}$</td>
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$^a$ $\gamma''$ and $\gamma'$ were fixed in the fit to the value (-0-0001 cm$^{-1}$ [17, 18]) from ESR experiments in rare gas matrices.
$^b$ In Ar matrices [32, 33].
$^c$ MP2/6-31G* [28, 29].
$^d$ UHF/6-31G* [28].
$^e$ UHF/4-21G [28].
$^f$ UHF/3-21G [23].
$^g$ MP2/4-21G [28].
$^h$ UHF/6-31G* [23].
$^i$ CASSCF [27].
$^j$ In Ar matrices [15, 16].
$^k$ In Ne matrices [15, 16].
$^l$ Ground state effective C--C bond length defined as $\frac{1}{8} \left\{ \frac{1}{2} (r_i + 2r_m + r_o) + \sqrt{\left(\frac{1}{2} (r_i + 2r_m + r_o)\right)^2 + \frac{3}{4} (r_i + 2r_m + r_o)^2} \right\}$ where $r_i$, $r_m$, and $r_o$ are the inner, middle, outer bond lengths.
(especially for $J = N$) but better reproduces the triplet fine structure splittings observed in the low $N$ transitions. The correlation matrix for the fit indicated that the upper and lower state constants are highly correlated (0.995, 0.996, and 0.978 for $B_v$, $D_v$, and $\lambda_v$, respectively). However, the correlations were completely removed when the data were fitted to the following modified set of molecular parameters: $B' - B''$, $D' - D''$, $\lambda - \lambda''$, $B''$, $D''$, $\lambda''$, and $\nu_4$. This indicates that the observed changes of the molecular parameters between the upper and lower states are determinable from the present data set.

As shown in table 2, no anomalous behaviour was detected in the molecular constants. The observed band origin is in good agreement with ab initio predictions. As suggested by Martin et al. [28] and also Kurtz and Adamowitz [29], the even-numbered clusters, C₄, C₆, and presumably C₈, would give a constant scaling factor between the calculated and measured frequencies for a similar type of vibration. Comparison of the present result with that of C₆ [13] for the highest frequency antisymmetric stretch fundamentals confirms this notion. The scaling factor is found to be almost exactly the same for both clusters, e.g. $\nu_{\text{exp}} / \nu_{\text{calc}} = 0.975$ and 0.976 for C₄ and C₆, respectively, for the MP2/6-31G* level of calculations [28, 29], and it is 0.890 and 0.895 for C₄ and C₆, respectively, for the UHF/6-31G* level [25, 28]. Using the scaling factor and the recent ab initio result for C₈ [29] for the MP2/6-31G* level, one can predict the highest frequency antisymmetric stretch fundamental of C₈ to be 2067 cm⁻¹. The observed band origin also confirms the systematic matrix induced red shift proposed previously by our group [11]. For the highest frequency antisymmetric stretch fundamentals of the linear C₃, C₅, C₇, and C₉ clusters, a near linear dependence between the matrix induced red shift and the cluster size was observed. The present result shows that the matrix shift is 7.9 cm⁻¹ for the $\nu_4 (\sigma_u)$ fundamental of C₆. This is almost exactly midway between those observed for C₅ (5.4 cm⁻¹) and C₇ (10.3 cm⁻¹).

The fact that the measured spin–spin interaction constant $\lambda_v$ compares well with the ESR results of Van Zee et al. [15, 16] from studies in rare gas matrices confirms their assignment of the ESR lines. The ESR values of $\lambda_v$ in rare gas matrices are found to be smaller than the gas phase value, showing a larger decrease in Ar than in Ne. This observed trend supports the matrix perturbation effect, originally proposed by Van Zee et al. [15] for C₆, and later adopted by Jiang and Graham [18] for C₄. It was suggested, based on the results for the CCO molecule [37], that the dominant matrix perturbation is the spin–orbit mixing of triplet and singlet states, which is enhanced by neighbouring rare gas atoms, resulting in a decrease in the matrix value of $\lambda_v$. Since this spin–orbit coupling is suggested [37] to be weaker in Ne than in Ar, the value of $\lambda_v$ in Ne is expected to be larger as observed in their experiments, and thus close to the gas phase value. This is confirmed in the present experiments.

4. Discussion

The present results support ab initio predictions of a linear C₆ cluster having cumulene-type bonding with a $^3\Sigma^-_g$ ground state. The fact that only odd rotational ($N$) levels were observed with triplet fine structure is in agreement with expected characteristics of a centrosymmetric linear triplet ($^3\Sigma^-_g$) carbon cluster. The excellent agreement between experiment and theory obtained for the ground state rotational constant and effective bond length also evidences the predicted linear structure. Nevertheless, the possibility of a slightly bent structure, as proposed for C₄ in rare gas matrices [17, 18], cannot be completely ruled out from the present
results. This is based on the following considerations. For a bent structure with a $C_2$ symmetry axis (i.e. either trans or cis geometry similar to those considered [30] for $C_4$), the $K_p = 0 \leftrightarrow 0$ rotational sub-band, whose components would have the strongest line intensities, can only produce $P$ and $R$ branches from odd $N$ levels due to the nuclear spin statistics and the selection rules. This transition characteristic is therefore identical to that of the linear structure. If the molecule were bent, however, one would expect to observe $K_p = 1 \leftrightarrow 1$ transitions with weaker intensities, as discussed previously [13] for $C_4$. Considering the selection rules and the nuclear spin statistics, it is expected that the $K_p = 1 \leftrightarrow 1$ transitions will give rise to all three ($P$, $Q$, and $R$) branches from both even and odd $N$ levels (this is qualitatively similar to what is expected for a bending hot band of $\pi-\pi$ type except for the shift of the band origin discussed below). It seems likely that some of the unassigned weak transitions mentioned earlier could belong to this type of transition. Our preliminary analysis suggests that about half of the approximately 80 unassigned lines can be attributed to two hot band series, presumably of $\pi-\pi$ type. They appear to result from both even and odd $N$ levels, and their band origins seems to be red shifted substantially (by a few wavenumbers) from the band origin reported here. Most of the remaining unassigned lines were observed in a narrow spectral region between $P(9)$ and $R(9)$ of the fundamental. This latter set of unassigned lines is suggestive of a $K_p = 1$ sub-band resulting from a bent structure, although it could certainly be another hot band. It is currently impossible to make definitive assignments for this sub-band due to the irregular spectrum pattern and low intensities. In this sub-band, transitions attributable to both even and odd $N$ levels have been observed. Moreover, their band origin seems to be very close to the band origin reported here (i.e. that of the $K_p = 0$ sub-band), since fine structure splittings, similar to those observed for the low $N$ transitions of the fundamental have been resolved for some of the transitions. This is different from the two hot band series discussed above, but in agreement with the expected small red shift of the band origin of the $K_p = 1$ sub-band compared with that of the $K_p = 0$ sub-band.

As discussed above, it is not possible given the present data set to make a definitive conclusion regarding a slight nonlinearity of the $C_6$ cluster. Simulations of the spectrum with a simple rigid rotor model (without taking into account the triplet fine structure splitting) indicate that the bending angle must be $5^\circ$ or smaller in order to reproduce the observed relative intensities of the $K_p = 0$ and 1 sub-bands, although more elaborate analysis, that includes assignments of the presumed $K_p = 1$ sub-band, would be necessary to examine more rigorously the possibility of a nonlinear structure. Moreover, we clearly cannot rule out the possibility of a quasilinear potential surface upon analysis of only a single rovibrational band. These interesting questions of nonlinearity and/or quasilinearity will certainly be addressed in future work. We strongly encourage theoretical efforts in these directions.

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References

[12] Heath, J. R., and Saykally, R. J., 1991, J. chem. Phys., 94, 3271. In this reference, the rovibrational transitions observed for the ν3(Ou ) fundamental of the linear 3EgC4 cluster were incorrectly assigned with only even N rotational quantum numbers. For the linear forms of both C2 and C6, the ground electronic state (3~) is antisymmetric and the nuclear spin state is symmetric with respect to interchange of the identical nuclei. Therefore, only odd N rotational levels are allowed in the ground state. A unit change in the N quantum number would correct the assignments, although more experimental data are necessary to make definitive assignments. Due to these misassignments, the molecular constants presented in this reference are slightly in error, but it does not materially affect the conclusions made in this work.