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# Fourier transform infrared isotopic study of the $C_{12}$ chain trapped in solid Ar

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A Fourier transform infrared investigation of the $^{13}C$ isotopic spectrum of linear $C_{12}$ in solid Ar coupled with density functional theory calculations at the B3LYP/cc-pVDZ level has resulted in the identification of the $\nu_8 = 1997.2$ and $\nu_9 = 1818.0\,\mathrm{cm}^{-1}$ stretching modes. Agreement between experimental measurements and theory is very good. The identification of a third mode $\nu_7 = 2140.6\,\mathrm{cm}^{-1}$ is considered tentative. © *2000 American Institute of Physics.* [S0021-9606(00)00710-8]

## I. INTRODUCTION

Although the spectra of carbon chains formed by trapping the products of the evaporation of graphite in matrices were first reported in the pioneering work of Weltner and McLeod[1] 35 years ago, experimental and theoretical work on carbon clusters continue unabated. These efforts are inspired by interest in understanding the structures and modes of formation of clusters ranging in size and complexity from the $C_4$ chain and $C_6$ ring ($D_{3h}$) to the fullerene structures. Further motivation is provided by the demonstrated role of carbon chains as interstellar and stellar molecular species and by suggestions that they may be the carriers of the diffuse interstellar bands.[2,3] The spectroscopy of carbon clusters was thoroughly reviewed by Weltner and Van Zee[4] in 1989. References to that and subsequent work appear in the database of vibrational and electronic energy level data compiled and critically evaluated by Jacox.[5]

In the case of linear $C_{12}$ Maier and co-workers[6] tentatively assigned frequencies at 2013.0 and 1819.5 cm$^{-1}$, which appeared on trapping the mass selected products from the laser evaporation of graphite in neon matrices and correlated with an absorption at 860.2 nm identified as the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ electronic transition of $C_{12}$. Later in a more extensive report on the infrared vibrations of mass-selected neutral and anion chains, they reported[7] three bands of which they assigned the two at 2012.6 and 1819.3 cm$^{-1}$ to $C_{12}^-$. Their revised assignments to the anion were based on a decrease in the intensity of the two absorptions observed on irradiation with light from a xenon arc lamp and on a correlation with the $^2\Pi_u \leftarrow X\,^2\Pi_g$ electronic transition of $C_{12}^-$ which they had measured previously.[6] In contrast, they reported that the third band at 2002.9 cm$^{-1}$ grew during photobleaching and thus tentatively attributed it to neutral $C_{12}$.

In theoretical work, density functional theory (DFT) calculations with both the BP (Ref. 8) (Becke–Perdew), B3LYP (Ref. 9) (Becke 3-parameter Lee–Yang–Parr), and LSD (Ref. 10) (local spin density) functionals, have indicated that a ring structure ($C_{6h}$) is more stable than the linear chain. For this reason, predictions of harmonic vibrational frequencies have focused on the cyclic structure.[8,9]

During previous FTIR (Fourier transform infrared) studies on cyclic $C_6$,[11] cyclic $C_8$,[12] and linear $SiC_9$,[13] formed by trapping the products from the laser evaporation of graphite and silicon rods in solid argon, we have noted that under conditions when $C_3$ is initially the dominant carbon molecule produced with perhaps some $C_9$, subsequent annealing of the matrix to ~40 K preferentially produces carbon clusters with multiples of the $C_3$ unit, specifically linear $C_6$,[14] cyclic $C_6$,[11] and linear $C_9$.[15] In conjunction with this preference we have noted the growth of a strong absorption at 1818.0 cm$^{-1}$, close to the 1819.3 cm$^{-1}$ frequency Maier's group[7] attributed to $C_{12}^-$ in a Ne matrix. These observations have prompted the present matrix FTIR and theoretical investigation of $^{13}C$ isotopic shifts for the carbon–carbon stretching fundamentals of linear $C_{12}$.

## II. THEORY

Theoretical predictions for isotopic shifts of fundamental vibrational frequencies can often be used successfully to aid in the identification of new molecular species. Previously we have also pointed out some of the problems of relying too blindly on such an approach.[12] In particular, for systems, which exhibit several vibrational fundamentals close in frequency, the perturbation introduced by the isotopic substitution may lead to strong interactions between these modes. In the case of linear carbon chains this situation is inevitable as the length of the chain increases. To further exacerbate (or complicate) the situation only isotopomers that break the $D_{\infty h}$ symmetry give rise to interactions between $\sigma_u$ and $\sigma_g$ modes. This makes it increasingly difficult to interpret a spectrum including highly substituted isotopomers since some isotopomers may remain unperturbed whereas others may be coupled strongly to other modes. To illustrate this situation and to aid in the identification of the vibrational spectrum of linear $C_{12}$ we have performed a series of density functional calculations at the standard B3LYP/cc-pVDZ level using the GAUSSIAN 94/DFT[16] program suite.

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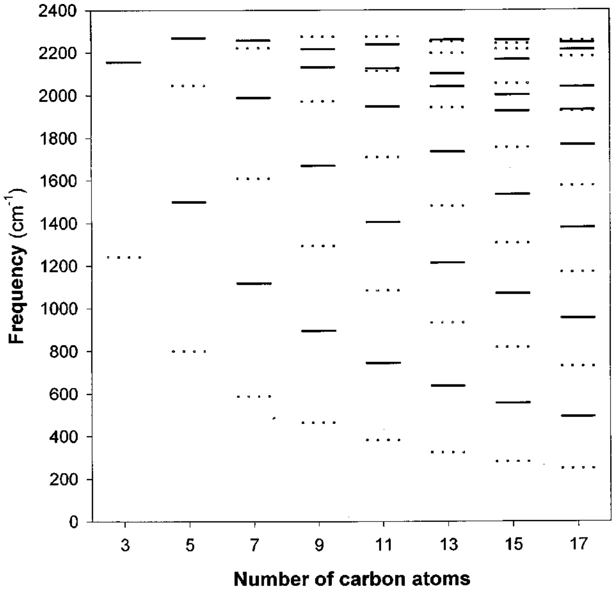

FIG. 1. Vibrational stretching frequencies for linear carbon chains with odd number of carbon atoms. Solid lines indicate $\sigma_u$ modes, dotted lines indicate $\sigma_g$ modes.

With an increasing number of carbons in a chain the density of vibrational fundamentals at high frequency increases. This is illustrated in Figs. 1 and 2 where the stretching fundamental frequencies obtained at the B3LYP/cc-pVDZ level have been plotted as a function of the number of carbon atoms for odd and even numbered clusters, respectively. For shorter chains, the modes are well separated in frequency with alternating $\sigma_u$ and $\sigma_g$ modes whereas for longer chains the situation becomes more complicated, particularly in the high frequency domain. This general behavior leads to some difficulties when trying to interpret the isotopic spectra of long carbon chains.

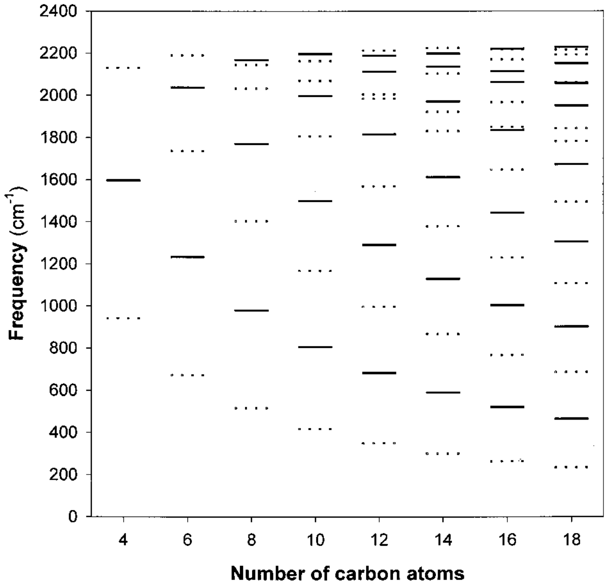

FIG. 2. Vibrational stretching frequencies for linear carbon chains with even number of carbon atoms. Solid lines indicate $\sigma_u$ modes, dotted lines indicate $\sigma_g$ modes.

To further analyze this situation we have previously introduced a perturbative treatment of isotopic shifts.[17] One can show that, working within the harmonic approximation, the first order singly substituted shift for a noninteracting vibrational frequency is given by

$$\Delta_1 = \frac{\omega}{2}\left(1 - \frac{m_i}{m_f}\right)|\mathbf{u}|^2 \equiv 2\omega\alpha|\mathbf{u}|^2, \tag{1}$$

where $m_i$ and $m_f$ are the initial and final isotopic masses, respectively, $\omega$ the fundamental frequency, and $\mathbf{u}$ is the mass weighted, zeroth-order normal mode coordinate for the isotopically substituted nucleus. To add the effects of interactions with other modes one can consider a first-order effective Hamiltonian matrix (see e.g., Ref. 12) with elements

$$(H_1^{\text{eff}})_{rs} = \omega_r \delta_{rs} - 2\sqrt{\omega_r \omega_s}\alpha \mathbf{u}_r \cdot \mathbf{u}_s\,. \tag{2}$$

This introduces a mixing of vibrational modes provided the scalar product between the atomic displacement vectors, $\mathbf{u}_r$ and $\mathbf{u}_s$, is nonzero. For linear $C_{12}$ this only introduces mixing between stretching modes since they are all perpendicular to the bending vibrations. Upon diagonalization of the matrix defined by Eq. (2), the frequencies obtained will effectively include higher-order contributions in the perturbation series. The magnitude of these contributions depend on the scalar product above as well as on the difference in frequency between the zeroth order fundamental frequencies. Since the isotopic shift can also be obtained to infinite order by diagonalization of the appropriately mass weighted force constant matrix one can easily get an estimate of the importance of higher-order contributions. We have previously introduced[12,15] a convenient measure of the relative importance, which we termed the isotopic sensitivity index, defined by

$$\iota_s \equiv \left|\frac{\Delta_2 + \Delta_3 + \cdots}{\Delta_1}\right| = \left|1 - \frac{\Delta_\infty}{\Delta_1}\right|, \tag{3}$$

where $\Delta_i$ denotes the isotopic shift to the $i$th order. A low value of the sensitivity index would indicate that a first-order treatment based on Eq. (1) should suffice for small mass perturbations whereas a larger value would indicate a substantial admixture of other vibrational modes. In the latter case calculated isotopic shifts would thus be more sensitive to the exact behavior of all vibrational fundamentals.

The perturbative analysis presented above can now be used as a guide when interpreting the isotopic spectrum of linear $C_{12}$. The optimized B3LYP/cc-pVDZ geometry parameters for the $^3\Sigma_g^-$ linear ground state of $C_{12}$ are given in Table I. Although the cyclic isomer of $C_{12}$ has been predicted to be the global ground state,[8,9] the linear structure is found to be a local minimum on the B3LYP/cc-pVDZ potential energy surface. The harmonic stretching fundamentals calculated at this level of theory, are given in Table II. We note that the $\nu_7(\sigma_u)$ mode is relatively close ($<25$ cm$^{-1}$) in frequency to the infrared inactive $\nu_1(\sigma_g)$ mode (see also Fig. 2). From our perturbative analysis, one can thus expect the calculated shifts, for this mode in particular, to display substantial errors as compared with experiment. Table III shows a comparison of the isotopic sensitivity index for single $^{13}$C substitution calculated with Eq. (3) for the five $\sigma_u$ modes of

TABLE I. B3LYP/cc-pVDZ optimized geometry parameters for $C_{12}$. The equilibrium rotational constant for this geometry is $B_e = 0.178$ GHz.

| Bond | Parameter value (Å) |
|---|---|
| C1–C2 | 1.300 |
| C2–C3 | 1.299 |
| C3–C4 | 1.280 |
| C4–C5 | 1.289 |
| C5–C6 | 1.282 |
| C6–C7 | 1.288 |

linear $C_{12}$. The sensitivity index behaves as expected in that it predicts a low sensitivity for the low frequency $\nu_{11}(\sigma_u)$ mode whereas it predicts a high sensitivity for the high frequency $\nu_7(\sigma_u)$ mode. Below we will link the behavior of the isotopic sensitivity index to the behavior of the experimental isotopic shifts.

## III. EXPERIMENTAL PROCEDURE

Matrix samples were prepared by vaporizing the surface of carbon rods using a slightly focused Nd:YAG (GCR-11, Spectra-Physics) pulsed laser operating at 1064 nm. The evaporated species were condensed in solid Ar (Matheson, 99.9995% purity) on a gold plated surface cooled to ~10 K by a closed cycle refrigerator (APD Cryogenics, Displex) in a vacuum of $10^{-7}$ torr or better during the experiment.

The carbon rods were fabricated by mixing carbon-12 (Alfa, 99.9995% purity) and carbon-13 (Isotec, 99.3% purity) powder in various ratios and then pressing the mixtures into rods. A degassing procedure was used to remove any trapped gas by heating the rods to ~200 °C under vacuum for 24 h.

During evaporation, a filter was used to prevent solid particles sputtered off the rod surface from reaching the deposition site. After the evaporation, thermally induced diffusion in the matrix was used to enable the growth of large clusters by warming the matrix to a specific temperature and maintaining it there for ~10 min before cooling back to ~10 K.

FTIR absorption spectra of the matrix samples were recorded in the region of 550–3900 $\mathrm{cm}^{-1}$ at a resolution of 0.2 $\mathrm{cm}^{-1}$ using a Bomem DA 3.16 Fourier transform spectrometer equipped with a liquid nitrogen cooled MCT (Hg–Cd–Te) detector and KBr beamsplitter. Details of the optical system have been reported previously.[18] The frequencies of all bands reported were measured to ±0.1 $\mathrm{cm}^{-1}$, unless unresolved because of overlapping absorptions.

TABLE II. B3LYP/cc-pVDZ harmonic frequencies and infrared intensities for all stretching modes of linear $C_{12}$.

| Vibrational mode | Frequency ($\mathrm{cm}^{-1}$) | Infrared intensity (km/mol) |
|---|---|---|
| $\nu_1(\sigma_g)$ | 2213 | 0 |
| $\nu_2(\sigma_g)$ | 2005 | 0 |
| $\nu_3(\sigma_g)$ | 1985 | 0 |
| $\nu_4(\sigma_g)$ | 1569 | 0 |
| $\nu_5(\sigma_g)$ | 997 | 0 |
| $\nu_6(\sigma_g)$ | 350 | 0 |
| $\nu_7(\sigma_u)$ | 2189 | 2406 |
| $\nu_8(\sigma_u)$ | 2113 | 4794 |
| $\nu_9(\sigma_u)$ | 1815 | 1191 |
| $\nu_{10}(\sigma_u)$ | 1290 | 121 |
| $\nu_{11}(\sigma_u)$ | 683 | 1.2 |

TABLE III. Comparison of the isotopic sensitivity index for single $^{13}C$ substitution for the $\sigma_u$ modes of linear $C_{12}$.

| $C_{12}$ Isotopomer C–C–C–C–C–C–⋯ | $\nu_7(\sigma_u)$ | $\nu_8(\sigma_u)$ | $\nu_9(\sigma_u)$ | $\nu_{10}(\sigma_u)$ | $\nu_{11}(\sigma_u)$ |
|---|---|---|---|---|---|
| 13–12–12–12–12–12–⋯ | <0.01 | 0.06 | <0.01 | 0.07 | 0.03 |
| 12–13–12–12–12–12–⋯ | <0.01 | 0.10 | 0.19 | 0.07 | <0.01 |
| 12–12–13–12–12–12–⋯ | 0.26 | 0.12 | 0.09 | 0.05 | 0.10 |
| 12–12–12–13–12–12–⋯ | <0.01 | 0.08 | 0.18 | 0.09 | 0.07 |
| 12–12–12–12–13–12–⋯ | 0.14 | 0.06 | 0.12 | 0.09 | <0.01 |
| 12–12–12–12–12–13–⋯ | 0.51 | <0.01 | 0.17 | 0.08 | 0.09 |
| RMS | 0.24 | 0.08 | 0.14 | 0.08 | 0.06 |

## IV. RESULTS AND DISCUSSION

Figures 3 and 4 show the absorptions at 1818.0 and 1997.2 $\mathrm{cm}^{-1}$, which are observed to grow in together during annealing for 10 min at 5 K increments from 20 to 35 K. Typically, spectra for these matrices initially show a strong $\nu_3 = 2038.9\ \mathrm{cm}^{-1}$ band of $C_3$ which slowly diminishes while strong absorptions indicative of linear $C_6$ ($\nu_4 = 1952.5\ \mathrm{cm}^{-1}$), cyclic $C_6$ ($\nu_3 = 1694.9\ \mathrm{cm}^{-1}$), and linear $C_9$ ($\nu_6 = 1998.0\ \mathrm{cm}^{-1}$) grow in, presumably formed by reactions of the $C_3$ units. The observed 1818.0 $\mathrm{cm}^{-1}$ absorption is fortuitously close to the frequency of one of the stretching modes $\nu_9 = 1817.8\ \mathrm{cm}^{-1}$ of linear $C_{12}$ predicted by B3LYP/cc-pVDZ DFT calculations. A second absorption at 1997.2 $\mathrm{cm}^{-1}$, which grows in simultaneously, is not as close to the frequency of 2112.3 $\mathrm{cm}^{-1}$ predicted for the $\nu_9$ mode, but is nevertheless a reasonable candidate. A detailed analysis of the $^{13}C$ isotopic shifts supports this contention.

Figure 3 shows the isotopic shifts which are observed as a result of the enrichment of the starting material for the graphite rod with 8% $^{13}C$. This level of enrichment is typically chosen for our studies of isotopic shifts in larger carbon clusters in order to limit isotopic substitutions to single carbon replacements only. This strategy reduces the number of isotopic shifts and the consequent confusion and error caused by matching a large number of closely packed and frequently overlapping bands with numerous shifts predicted by theory in a fairly confined frequency region. The smaller number of shifts resulting from single substitutions then provides a critical test for an unambiguous identification of the cluster in question.[15,19]

In Fig. 3, four isotopomer shifts are readily observed to the low frequency side of the 1818.0 $\mathrm{cm}^{-1}$ absorption, which grow in together with the main band during annealing and, consistent with the level of $^{13}C$ enrichment, are ~8–10% as intense. A fifth band at 1813.4 $\mathrm{cm}^{-1}$ with an integrated intensity consistently twice that of the others is revealed under the optimum conditions of Fig. 3 to actually consist of two overlapping bands at 1813.3 and 1813.6 $\mathrm{cm}^{-1}$. The six shifts

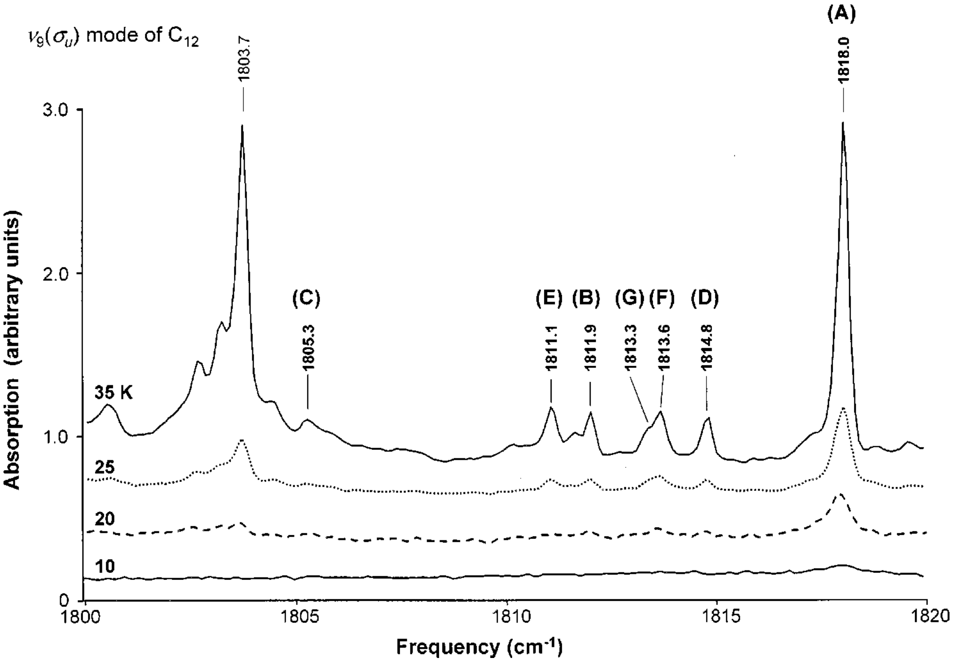

FIG. 3. FTIR spectra of the proposed $\nu_9(\sigma_u)$ mode of $C_{12}$ and its $^{13}C$ isotopic shifts produced by the laser evaporation of a mixture of 8% $^{13}C$ and 92% $^{12}C$. Spectra were recorded after trapping the products in Ar at ~10 K and following annealing at 20, 25, and 35 K. The letters correspond to the single $^{13}C$ substituted isotopomers listed in Table IV.

thus observed are consistent with a chain of 12 carbon atoms. The specific single $^{13}C$ isotopomers responsible for the absorptions are designated by the letters B–G in Fig. 3 and are identified in Table IV.

As can be seen in Table IV, comparison of the observed shifts with the scaled predictions of the B3LYP/cc-pVDZ DFT calculations for single $^{13}C$ substitutions for the $\nu_9(\sigma_u)$ mode of linear $C_{12}$ shows reasonably good agreement with all but one assignment showing a difference between theory and experiment of $<1$ cm$^{-1}$. It should be noted that the assignment of the 1811.9 and 1813.3 cm$^{-1}$ absorptions to the B and G isotopomers, respectively, rather than the reverse, is guided by the sensitivity indices shown in Table III. The smallest discrepancy between experiment and theory in Table IV (0.0 cm$^{-1}$) occurs for the 1811.9 cm$^{-1}$ band assigned to the B isotopomer and is consistent with the conclusion that because of the very small sensitivity index ($<0.01$) for this isotopomer in Table III, the theoretical prediction should be reliable. The largest discrepancy of 2.0 cm$^{-1}$, which is observed for the assignment of the 1813.3 cm$^{-1}$ band to the G isotopomer, is consistent with its relatively larger isotopic sensitivity index and the consequent lower reliability of theory for this shift. Also contributing to the discrepancy may be greater experimental uncertainty in the frequency of the 1813.3 cm$^{-1}$ band because of its overlap with the 1813.6 cm$^{-1}$ absorption.

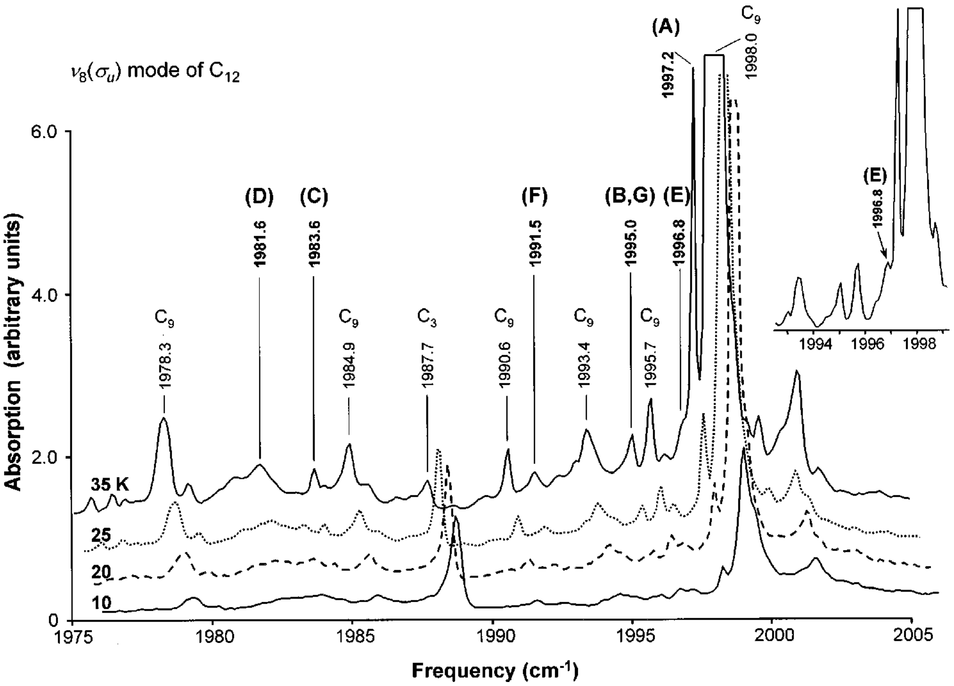

FIG. 4. FTIR spectra of the proposed $\nu_g(\sigma_u)$ mode of $C_{12}$ and its $^{13}C$ isotopic shifts produced by the laser evaporation of a mixture of 8% $^{13}C$ and 92% $^{12}C$. Spectra were recorded after trapping the products in Ar at ~ 10 K and following annealing at 20, 25, and 35 K. The letters correspond to the single $^{13}C$ substituted isotopomers listed in Table V. The spectra recorded on deposition (~ 10 K) and after annealing to 20 and 25 K have been displaced to higher frequency to facilitate comparison.

TABLE IV. Comparison of observed vibrational frequencies ($cm^{-1}$) of the $\nu_9(\sigma_u)$ mode for single $^{13}C$-substituted isotopomers of $C_{12}$ with the predictions of B3LYP/cc-pVDZ calculations.

| $C_{12}$ Isotopomer C–C–C–C–C–C–··· | | Observed $\nu$ | B3LYP/ cc-pVDZ $\nu$ | Scaled[a] $\nu$ | Difference $\Delta\nu$ |
|---|---|---|---|---|---|
| 12–12–12–12–12–12–··· | (A) | 1818.0 | 1815.1 | 1818.0 | |
| 13–12–12–12–12–12–··· | (B) | 1811.9 | 1809.0 | 1811.9 | 0.0 |
| 12–13–12–12–12–12–··· | (C) | 1805.3 | 1803.3 | 1806.2 | 0.9 |
| 12–12–13–12–12–12–··· | (D) | 1814.8 | 1812.3 | 1815.2 | 0.4 |
| 12–12–12–13–12–12–··· | (E) | 1811.1 | 1807.8 | 1810.7 | −0.4 |
| 12–12–12–12–13–12–··· | (F) | 1813.6 | 1809.8 | 1812.7 | −0.9 |
| 12–12–12–12–12–13–··· | (G) | 1813.3 | 1808.4 | 1811.3 | −2.0 |

[a] Results of the B3LYP/cc-pVDZ calculation scaled by a factor of 1.0016.

TABLE V. Comparison of observed vibrational frequencies ($cm^{-1}$) of the $\nu_8(\sigma_u)$ mode for single $^{13}C$-substituted isotopomers of $C_{12}$ with the predictions of B3LYP/cc-pVDZ calculations.

| $C_{12}$ Isotopomer C–C–C–C–C–C–··· | | Observed $\nu$ | B3LYP/ cc-pVDZ $\nu$ | Scaled[a] $\nu$ | Difference $\Delta\nu$ |
|---|---|---|---|---|---|
| 12–12–12–12–12–12–··· | (A) | 1997.2 | 2112.9 | 1997.2 | |
| 13–12–12–12–12–12–··· | (B) | 1995.0 | 2110.6 | 1995.0 | 0.0 |
| 12–13–12–12–12–12–··· | (C) | 1983.6 | 2098.8 | 1983.9 | 0.3 |
| 12–12–13–12–12–12–··· | (D) | 1981.6 | 2096.7 | 1981.9 | 0.3 |
| 12–12–12–13–12–12–··· | (E) | 1996.8 | 2112.5 | 1996.8 | 0.0 |
| 12–12–12–12–13–12–··· | (F) | 1991.5 | 2107.1 | 1991.7 | 0.2 |
| 12–12–12–12–12–13–··· | (G) | 1995.0 | 2110.5 | 1994.9 | −0.1 |

[a] Results of the B3LYP/cc-pVDZ calculation scaled by a factor of 0.94523.

Figure 4 shows a band at 1997.2 $cm^{-1}$, which as indicated by comparison with Fig. 3 grows in with the $\nu_9(\sigma_u)$ mode at 1818.0 $cm^{-1}$. This new band thus becomes a candidate for the second of the three intense stretching modes predicted by DFT theory, $\nu_8(\sigma_u)$ at 2112.9 $cm^{-1}$. As indicated in Fig. 4 the nearby $\nu_6(\sigma_u)$ mode of $C_9$ at 1998.0 $cm^{-1}$ and its single $^{13}C$ substituted isotopomer bands complicate this region of the spectrum. However, as shown, when the $C_9$ isotopomer bands[15,20] are eliminated, another series of isotopomer bands, which grow in with the 1997.2 $cm^{-1}$ band, are readily identified (features B–G in Fig. 4). The 1995 $cm^{-1}$ absorption is twice as intense as the well-resolved C and F isotopomer bands because it consists of overlapping shifts for the B and G isotopomers. The 1996.8 $cm^{-1}$ absorption, which appears as a shoulder in the top spectrum in Fig. 4, is in other spectra resolved as a separate band (see inset). It is worth emphasizing that the 1997.2 $cm^{-1}$ band and its isotopic shifts increase in intensity as the $\nu_6(\sigma_u)$ mode of $C_9$ decreases during extreme annealing, presumably as some $C_9$ participates in reactions to form $C_{12}$. In contrast, the initial deposition of low concentrations of $C_3$ and $C_9$ in the preannealed sample, which by this argument would be expected to reduce the production of $C_{12}$, results in little or no absorption at 1997.2 $cm^{-1}$.

Comparison of the frequencies of the observed isotopic shifts with the scaled predictions of the DFT calculations for the $\nu_8(\sigma_u)$ mode of $C_{12}$ is shown in Table V. The agreement with theory is very good, with all differences being $\leqslant 0.3$ $cm^{-1}$. The smaller discrepancies between theory and experiment for $\nu_8$ compared to $\nu_9$ are consistent with the conclusion drawn from Table III that, because of the smaller sensitivity indices for the former mode, the predicted isotopic shifts for it should be more reliable.

The third stretching vibration of $C_{12}$ predicted to have observable intensity is the $\nu_7(\sigma_u)$ mode at 2189.1 $cm^{-1}$. Figure 5 shows an absorption band at 2140.6 $cm^{-1}$, which grows in with the $\nu_8$ and $\nu_9$ modes of $C_{12}$ already identified. Also exhibited are four potential isotopomer shifts labeled D–G. As can be seen in Table VI, the frequencies of these four absorptions agree reasonably well with the predictions of the DFT calculations for four of the singly substituted $^{13}C$ isotopomers of $C_{12}$. Several factors, however, tend to make

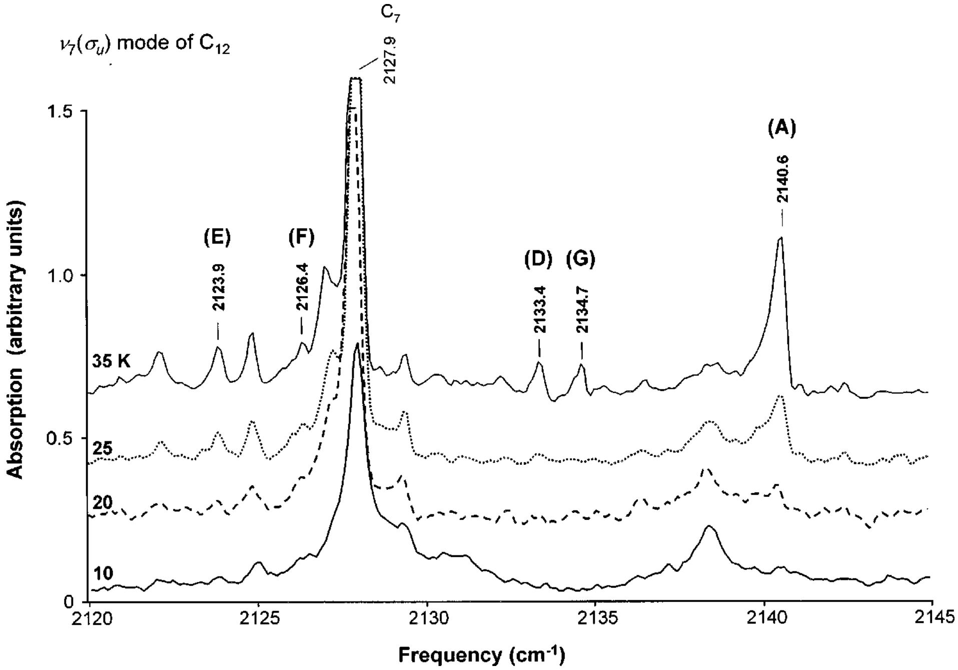

FIG. 5. FTIR spectra of the proposed $\nu_7(\sigma_u)$ mode of $C_{12}$ and its $^{13}C$ isotopic shifts produced by the laser evaporation of a mixture of 8% $^{13}C$ and 92% $^{12}C$. Spectra were recorded after trapping the products in Ar at ~10 K and following annealing at 20, 25, and 35 K. The letters correspond to the single $^{13}C$ substituted isotopomers listed in Table VI.

TABLE VI. Comparison of observed vibrational frequencies ($cm^{-1}$) of the $\nu_7(\sigma_u)$ mode for single $^{13}C$-substituted isotopomers of $C_{12}$ with the predictions of B3LYP/cc-pVDZ calculations.

| $C_{12}$ Isotopomer<br>C–C–C–C–C–C–··· | | Observed<br>$\nu$ | B3LYP/<br>cc-pVDZ<br>$\nu$ | Scaled[a]<br>$\nu$ | Difference<br>$\Delta\nu$ |
|---|---|---|---|---|---|
| 12–12–12–12–12–12–··· | (A) | 2140.6 | 2189.1 | 2140.6 | |
| 13–12–12–12–12–12–··· | (B) | ··· | 2189.1 | 2140.6 | ··· |
| 12–13–12–12–12–12–··· | (C) | ··· | 2189.0 | 2140.5 | ··· |
| 12–12–13–12–12–12–··· | (D) | 2133.4 | 2182.6 | 2134.3 | 0.9 |
| 12–12–12–13–12–12–··· | (E) | 2123.9[b] | 2172.1 | 2124.0 | 0.1 |
| 12–12–12–12–13–12–··· | (F) | 2126.4[b] | 2174.6 | 2126.4 | 0.0 |
| 12–12–12–12–12–13–··· | (G) | 2134.7 | 2184.4 | 2136.0 | 1.3 |

[a] Results of the B3LYP/cc-pVDZ calculation scaled by a factor of 0.97784.
[b] Assignments doubtful. See text for discussion.

the assignment of the 2140.6 $cm^{-1}$ absorption to the $\nu_7(\sigma_u)$ mode somewhat uncertain. The isotopic shift data is limited because the predicted shifts of 0.0 and 0.1 $cm^{-1}$ for the two other isotopomers [(B) and (C)] place them within the envelope of the 2140.6 $cm^{-1}$ main absorption, rendering them unobservable. In addition, careful examination of the spectra in Fig. 5 recorded as the sample was annealed indicates that absorptions E and F appear to have grown more quickly than the main band and the candidates for its isotopomer bands, D and G. In the case of the F band this may in part be an effect of overlap by the nearby $\nu_4(\sigma_u)$ mode of $C_7$ (Ref. 14) at 2127.9 $cm^{-1}$ which also grows in on annealing. Similarly, the E band already appears to be growing in after 20 K annealing when the main band (A) is still very weak. However, the presence of another weak feature in the vicinity after 25 K annealing may indicate that the anomalously high intensity of E is again the result of overlap with an unrelated feature. Further uncertainty in the assignment is contributed by the conclusion from sensitivity indices in Table III that the theoretical shifts are likely to be relatively less reliable for this mode. In view of these reservations the assignment of the 2140.6 $cm^{-1}$ absorption to the $\nu_7(\sigma_u)$ mode must be considered tentative.

Based on the assignments of isotopic shifts presented in Tables IV–VI we can now compare the absolute value of the errors relative to the predicted shifts and the values for the isotopic sensitivity index in Table III. Figure 6 shows the expected increase in the scatter of errors with an increase in the isotopic sensitivity index. The behavior shown in this graph is consistent with our previous experience, where as a rule of thumb an absolute error of $\leqslant 0.5$ $cm^{-1}$ can be expected for an isotopic sensitivity less than 0.1.

As can be seen from Table II, the DFT calculations predict relative intensities of 0.50, 1.00, and 0.25 for $\nu_7$, $\nu_8$, and $\nu_9$, respectively, compared with measured relative intensities of 0.13, 1.00, and 0.57 for the proposed assignments $\nu_7 = 2140.6$, $\nu_8 = 1997.2$, and $\nu_9 = 1818.0\,cm^{-1}$. (It should be noted that the spectra in Figs. 4–6 are all plotted to the same scale to facilitate comparison of the band intensities.) The $\nu_8$ mode is thus observed to be the most intense, in agreement with theory; however, the discrepancy between the relative intensities of the other two modes is well within the differences between DFT intensity predictions and measured values typically found for carbon chains.

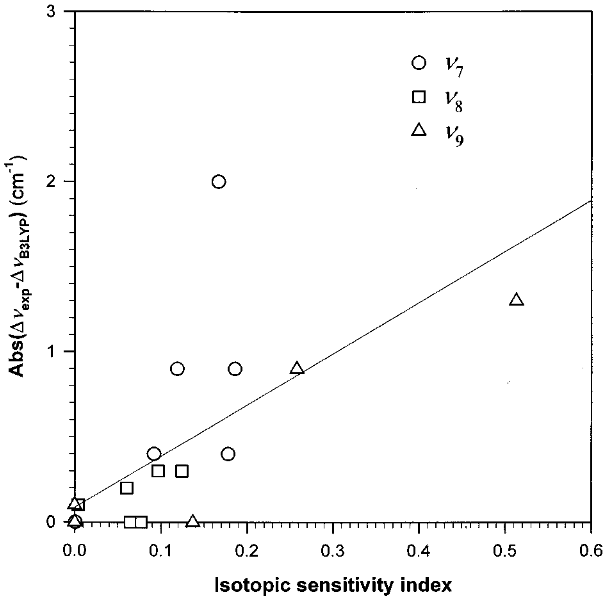

FIG. 6. Absolute error between observed and calculated (B3LYP/-cc-pVDZ) isotopic shifts for the $\nu_7(\sigma_u)$, $\nu_8(\sigma_u)$, and $\nu_9(\sigma_u)$ modes of $C_{12}$ as a function of the isotopic sensitivity index.

Our proposed assignments for the $\nu_7$, $\nu_8$, and $\nu_9$ vibrational modes for $C_{12}$ trapped in an Ar matrix can be compared with the previous assignments by Maier's group[6,7] for $C_{12}$ and $C_{12}$ trapped in Ne. Almost certainly, our $\nu_9 = 1818.0\,cm^{-1}$ mode for $C_{12}$ corresponds to their 1819.3 $cm^{-1}$ band which they observed in Ne and tentatively assigned to $C_{12}^-$ on the basis of behavior in their photobleaching experiment. It is also probable that our $\nu_8 = 1997.2\,cm^{-1}$ mode corresponds to their 2012.6 $cm^{-1}$ absorption, which they also tentatively assigned to the anion based on its similar behavior to their 1819.2 $cm^{-1}$ absorption. We can find no evidence, however, in our experiments for assigning the $\nu_9 = 1818.0$ and $\nu_8 = 1997.2\,cm^{-1}$ bands to $C_{12}^-$. It is also important to note the at least 100-fold increase in the intensity of these bands typically observed on annealing (see Figs. 3–5). This behavior appears very unlikely if their carrier is the anion. Certainly, our experiment was not designed with a source of electrons to produce anions, and none of the vibrations of other ions, such as $C_3^-$ and $C_6^-$ which have been previously identified and had their $^{13}C$ shifts measured,[7,21,22] appear in our spectra. A counter argument to this latter point is that laser evaporation by itself has produced electrons and hence ions in other systems, and that the higher electron affinity for longer carbon chains, such as $C_{12}$, may enable the unanticipated formation of their anions. For this reason therefore, we have further explored this possibility by comparing our experimental spectra with the predictions of DFT calculations for $C_{12}^-$.

Table VII shows B3LYP/cc-pVDZ harmonic frequencies and infrared intensities for all the stretching modes of the $C_{12}^-$ anion. It is worth noting that the frequencies of the three $C_{12}^-$ anion modes predicted to be the most intense $\nu_7(\sigma_u) = 2197$, $\nu_8(\sigma_u) = 2124$, and $\nu_9(\sigma_u) = 1902\,cm^{-1}$ differ from the observed frequencies 2140.6, 1997.2, and

TABLE VII. B3LYP/cc-pVDZ harmonic frequencies and infrared intensities for all stretching modes of the $^2\Pi_g$ of linear $C_{12}^-$.

| Vibrational mode | Frequency ($cm^{-1}$) | Infrared intensity (km/mol) |
|---|---|---|
| $\nu_1(\sigma_g)$ | 2216 | 0 |
| $\nu_2(\sigma_g)$ | 2039 | 0 |
| $\nu_3(\sigma_g)$ | 1990 | 0 |
| $\nu_4(\sigma_g)$ | 1537 | 0 |
| $\nu_5(\sigma_g)$ | 982 | 0 |
| $\nu_6(\sigma_g)$ | 344 | 0 |
| $\nu_7(\sigma_u)$ | 2197 | 2985 |
| $\nu_8(\sigma_u)$ | 2124 | 3761 |
| $\nu_9(\sigma_u)$ | 1902 | 1346 |
| $\nu_{10}(\sigma_u)$ | 1272 | 12 |
| $\nu_{11}(\sigma_u)$ | 671 | 53 |

1818.0 $cm^{-1}$, by 56, 128, and 84 $cm^{-1}$, respectively. By comparison the differences between the observed frequencies and those predicted for the neutral $C_{12}$ modes, $\nu_7(\sigma_u)=2189$, $\nu_8(\sigma_u)=2113$, and $\nu_9(\sigma_u)=1815\,cm^{-1}$, are 48, 115, and $\sim$0 $cm^{-1}$, respectively. There is thus on this basis no significantly better fit for one over the other. Empirically an approximate linear relationship is found between experimental frequencies and calculated harmonic stretching frequencies for linear carbon chains. The scaling factors used to bring calculated frequencies in line with experimental data are thus found to fall within a relatively narrow range (e.g., for B3LYP/cc-pVDZ calculations the scaling factors fall within 0.93–0.98 for previously identified linear carbon chain stretching fundamentals). Such considerations are helpful to find an expected range of experimental frequencies from given calculated harmonic values. However, it is likely that as linear chains grow longer one will observe an increase in the spread of such scaling factors due to the growing number of vibrational modes.

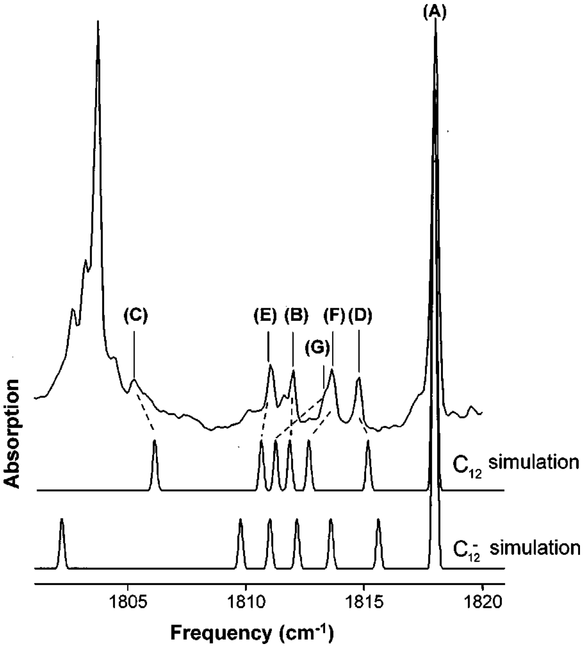

FIG. 7. Comparison of observed FTIR spectrum (top) showing singly substituted isotopic shifts with the simulated spectrum of the $\nu_9(\sigma_u)$ mode of neutral $C_{12}$ (middle) based on the B3LYP/cc-pVDZ calculation, and also with the simulated spectrum of the $\nu_9(\sigma_u)$ mode of anion $C_{12}^-$ (bottom) based on the B3LYP/cc-pVDZ calculation. The letters correspond to the single $^{13}C$ substituted isotopomers listed in Table IV.

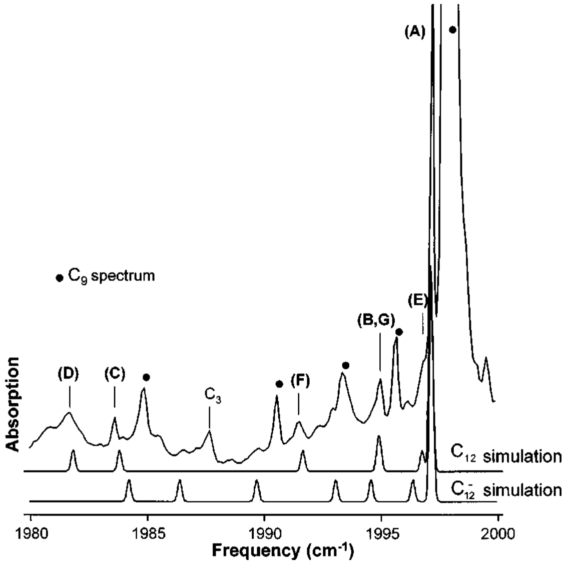

FIG. 8. Comparison of observed FTIR spectrum (top) showing singly substituted isotopic shifts with the simulated spectrum of the $\nu_8(\sigma_u)$ mode of neutral $C_{12}$ (middle) based on the B3LYP/cc-pVDZ calculation, and also with the simulated spectrum of the $\nu_8(\sigma_u)$ mode of anion $C_{12}^-$ (bottom) based on the B3LYP/cc-pVDZ calculation. The letters correspond to the single $^{13}C$ substituted isotopomers listed in Table V.

A more decisive test is provided by comparing the isotopic shifts predicted for the $C_{12}$ neutral and for the anion with our observed spectra. The results support the conclusion that the observed absorptions belong to neutral $C_{12}$. Figures 7–9 show simulated isotopic spectra for the three modes of the $C_{12}^-$ anion along with the experimentally observed spectra. Also shown for comparison are the corresponding simu-

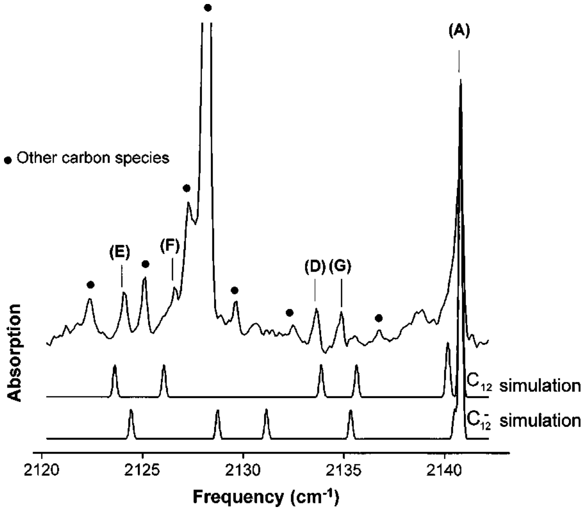

FIG. 9. Comparison of observed FTIR spectrum (top) showing singly substituted isotopic shifts with the simulated spectrum of the $\nu_7(\sigma_u)$ mode of neutral $C_{12}$ (middle) based on the B3LYP/cc-pVDZ calculation, and also with the simulated spectrum of the $\nu_7(\sigma_u)$ mode of anion $C_{12}^-$ (bottom) based on the B3LYP/cc-pVDZ calculation. The letters correspond to the single $^{13}C$ substituted isotopomers listed in Table VI.

lated isotopic spectra for the $\nu_7$, $\nu_8$, and $\nu_9$ modes of neutral $C_{12}$. As discussed earlier in connection with Table IV, the fit of the shifts predicted for the $\nu_9(\sigma_u)$ mode of $C_{12}$ with the observed shifts for our 1818.2 $cm^{-1}$ absorption is good (see Fig. 7). The predicted pattern of isotopic absorptions for $C_{12}^-$, is more widely dispersed than the observed spectrum, with larger deviations from the observed frequencies, and there is no suitable absorption for the (C) isotopomer. Similarly, in Fig. 8 the simulated isotopic spectrum for the $\nu_8(\sigma_u)$ mode of $C_{12}$ fits the observed spectrum for the 1997.2 $cm^{-1}$ band very well as could be expected from the excellent agreement between observed and calculated shifts noted earlier in Table V. The 2140.6 $cm^{-1}$ band which we have tentatively assigned to the $\nu_7$ mode of $C_{12}$ was not reported in earlier work by Maier;[6,7] however, this is probably explained by its being the weakest of the three. As demonstrated by Fig. 9, however, its isotopic spectrum is in good agreement with the simulation for $C_{12}$, and is clearly inconsistent with an assignment to the $C_{12}^-$ mode.

## V. CONCLUSION

C–C stretching modes of linear $C_{12}$ have been identified using FTIR isotopic shift measurements on single $^{13}C$ substituted isotopomers trapped in Ar matrices in conjunction with DFT calculations at the B3LYP/cc-pVDZ level. Measurements for the $\nu_9$ and $\nu_8$ modes at 1818.0 and 1997.2 $cm^{-1}$ are consistent with the theoretical predictions. The $\nu_7$ mode has been tentatively identified at 2140.6 $cm^{-1}$.

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