Reply to Comment on: Study of C_6^- and C_6 with threshold photodetachment spectroscopy and autodetachment spectroscopy

Caroline C. Arnold and Daniel M. Neumark
Department of Chemistry, University of California, Berkeley, California 94720
and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 24 March 1993; accepted 5 April 1993)

The Comment by Liu and Zhou consists of an *ab initio* calculation of the vibrational frequencies of C_6. Their calculated frequencies for the two lower frequency symmetric stretch modes (the ν_2 and ν_3 modes) are significantly higher than the experimental values[1] of 1322 and 489 cm^{-1} obtained from our threshold photodetachment spectrum of C_6^- [from peaks G and D, respectively; Fig. 4(a) in our paper]. On the basis of their results, which are similar to the calculated values of Martin and co-workers,[2] they conclude that our assignment of these modes is "too low" and "may not be due to fundamental vibrations of the ground state of linear C_6." These somewhat ambiguous comments can be addressed as follows.

The assignment of the features in our spectrum to linear C_6 is discussed at length in our paper. It is based on (i) the electron affinity, which agrees with the *ab initio* predictions of Bartlett,[3] (ii) the spin–orbit fine structure, which is consistent with a transition between a linear anion and linear neutral, and (iii) the observation of progressions in three different modes of the neutral, consistent with the three totally symmetric modes of linear C_6. (One expects transitions involving totally symmetric modes to dominate in a photodetachment spectrum.) In addition, our value for the highest frequency symmetric stretch mode (2061 cm^{-1}, from peak I) is in agreement with the *ab initio* value of Martin as well in this Comment. The features we see are clearly due to the ground state of linear C_6 because no transitions to lower lying states were seen in the anion photoelectron spectrum.[4]

The other interpretation of their Comment is that the peaks in question are due to linear C_6, but do not correspond to fundamental vibrational frequencies. We assume this means they would be due to $\Delta v=2$ transitions in low frequency non-totally symmetric modes (i.e., bending modes). Since Liu and Zhou presumably have a complete set of *ab initio* frequencies, they should have been able to test this possibility. Based on Martin's calculated frequencies, peak G cannot be matched to any such transition. From Martin's frequency of 223 cm^{-1} for the ν_7 (Π_g) bending mode, one could possibly assign peak D in our spectrum to the $\Delta v_7=2$ rather than the $\Delta v_3=1$ transition on the basis of position alone. However, in the absence of a symmetry change between the anion and neutral, peak D is far too intense for $\Delta v=2$ transition in a non-totally symmetric mode; according to Herzberg,[5] even if the ν_7 frequencies in the anion and neutral differ by a factor of 2, peak D should only have 5% of the intensity of the origin transition instead of 30%, as we observe.

Finally, we point out that if Liu and Zhou's symmetric stretch frequencies for the ν_2 and ν_3 modes are correct, then one must ask why the corresponding transitions do not appear in the zero electron kinetic energy (ZEKE) spectrum. This could only be the case if, upon photodetachment, no geometry change occurs along Q_2 and Q_3, the corresponding normal coordinates. Head-Gordon[6] has recently calculated anion and neutral geometries at the MP2/6-31G* level, and simulations using his results show significant activity in the ν_1 and ν_2 modes, while simulations using Adamowicz's *ab initio* geometries[7] show activity in all three symmetric stretch modes. We note that the anion bond lengths proposed in our paper for the anion to explain the experimental peak intensities are intermediate between values obtained by Head-Gordon and Adamowicz. In any case, it certainly seems that one or both of the modes in question should be sufficiently active to appear in the experimental spectrum.

Although we believe our symmetric stretch frequencies are correct, there remain some puzzling issues concerning the vibrations of C_6. In our paper, we pointed out that we could not come up with a reasonable set of force constants which reproduced our values for the symmetric stretch frequencies and the two literature values[8] for the antisymmetric stretch frequencies ($\nu_4=1952$ cm^{-1} and $\nu_5=1159$ cm^{-1}). The ν_4 value had received further support from isotopic substitution studies[9] prior to our paper, so we speculated that the ν_5 value might be incorrect. However, as Liu and Zhou point out, Graham[10] has very recently published matrix isolation spectroscopy results incorporating extensive isotopic substitution which confirm the ν_5 value. One possible explanation of this apparent inconsistency is that some of the vibrations in C_6 are sufficiently anharmonic that a harmonic force constant analysis is inappropriate. This would also explain why some of the *ab initio* frequencies are too high, since the calculated value assume harmonic potentials. In any case, we would certainly like to see more experimental and theoretical work on C_6 to resolve these issues.

This research is supported by the National Science Foundation under Grant No. DMR-9201159.

---

[1] C. C. Arnold, Y. Zhao, T. N. Kitsopoulos, and D. M. Neumark, J. Chem. Phys. 97, 6121 (1992).

[2] J. M. L. Martin, J. P. Francois, and R. Gijbels, J. Chem. Phys. 93, 8850 (1990).

0021-9606/93/99(2)/1442/2/$6.00

[3] J. D. Watts and R. J. Bartlett, J. Chem. Phys. **97**, 3445 (1992).

[4] S. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **144**, 431 (1988); D. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, J. Chem. Phys. **95**, 8753 (1991).

[5] G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966), p. 150.

[6] M. Head-Gordon (private communication). His bond lengths (in Å) are as follows: C_6: $r_a=1.303$, $r_b=1.296$, $r_c=1.282$. C_6^-: $r_a=1.277$, $r_b=1.332$, $r_c=1.265$.

[7] L. Adamowicz, Chem. Phys. Lett. **182**, 45 (1991); J. Kurtz and L. Adamowicz, Astrophys. J. **370**, 784 (1991).

[8] W. Weltner and R. J. Van Zee, Chem. Rev. **89**, 1713 (1989).

[9] M. Vala, T. M. Chandresekhar, J. Szczepanski, and R. Pellow, High Temp. Sci. **27**, 19 (1990).

[10] R. H. Kranze and W. R. M. Graham, J. Chem. Phy. **98**, 71 (1993).