

Lawrence Berkeley National Laboratory

Recent Work

Title

VIBRATIONAL FREQUENCIES OF SMALL METAL CLUSTERS. THE BERYLLIUM TETRAMER

Permalink

<https://escholarship.org/uc/item/8t77f1j5>

Author

Schaefer, H.F.

Publication Date

1985-05-01

2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY
AUG 2 1985
LIBRARY AND
DOCUMENTS SECTION

Presented at The Hawaii Nobel Laureate
Symposium, Honolulu, HI, December 16-22, 1984

VIBRATIONAL FREQUENCIES OF SMALL METAL CLUSTERS.
THE BERYLLIUM TETRAMER

R. Murphy and H.F. Schaefer III

May 1985

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks.



LBL-19875
2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

VIBRATIONAL FREQUENCIES OF SMALL METAL CLUSTERS.
THE BERYLLIUM TETRAMER

Robert Murphy and Henry F. Schaefer III
Department of Chemistry and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT. The structure and harmonic vibrational frequencies of Be_4 have been predicted using ab initio molecular electronic structure theory. A better than double zeta plus polarization (DZ+P) basis set was used in conjunction with self-consistent-field (SCF) and configuration interaction (CI) methods. The predicted frequencies (SCF followed by CI in parentheses) are a_1 651 (680), t_2 576 (589), and e 489 (487) cm^{-1} , respectively.

INTRODUCTION

During the past two years, the generation of well-defined metal clusters in the gas phase has progressed from dream to reality [1-6]. It is now becoming possible to study both the spectroscopic properties [1-3] and reactivity [4-6] of such small metal clusters. One of the primary motivations for the preparation of such "naked" clusters is to attempt to make analogies with metal surfaces and with metal particles involved in heterogeneous catalysis [7].

One of the simplest metal clusters to be well-characterized theoretically is the beryllium tetramer, Be_4 . It was established [8] in 1975 that Be_4 has a tetrahedral equilibrium geometry and is much more strongly bound than Be_2 or Be_3 . Subsequent theoretical studies [9-19] have confirmed this view and provided quantitatively reliable predictions. For example, Bauschlicher, Bagus, and Cox [17] have

addressed the problem using a triple zeta plus double polarization (TZ+2P) basis in conjunction with configuration interaction (CI) including all single and double excitations [20]. After appendage of the Davidson correction for quadruple excitations [21], the Be-Be bond distance was predicted to be 2.07 Å and the dissociation energy D_e to be 64 kcal/mole.

Vibrational spectroscopy has in recent years become a powerful tool for the characterization of metal surfaces and of chemisorption on metal surfaces [22]. In light of the analogy between surfaces and gas-phase metal clusters [7], it is apparent that the vibrational spectroscopy of the latter will in time become an important area of research. Since experimental studies of the infrared and Raman spectra of naked metal clusters are essentially nonexistent, theory is in a good position to provide some potentially helpful guidance to laboratory research. In this vein, we report here a theoretical study of the vibrational frequencies of Be_4 , a simple, relatively stable metal cluster.

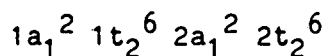
THEORETICAL APPROACH

Previous theoretical research has shown [14,17,19] that the reliable prediction of the dissociation energy of Be_4 , namely $\Delta E(\text{Be}_4 \rightarrow 4\text{Be})$, requires a high level of theory. Specifically, d orbitals must be included in the basis set, and the effects of electron correlation must be carefully considered.

Two basis sets of contracted gaussian functions were used in the present research and are designated A and B in Table 1. The Be s primitive functions are those of van Duijneveldt [23], truncated to four significant figures in the orbital exponents. This s basis is contracted to (9s/5s) so as to maintain maximum flexibility in the valence shell. The Be p functions are those optimized by Yarkony [24] for the lowest 3P state (electron configuration $1s^2 2s 2p$) of the atom. As seen in Table 1, the p basis functions are contracted

(4p/2p) in Basis A and (4p/3p) in Basis B. Both basis sets include a set of six d-like functions (x^2 , y^2 , z^2 , xy , xz , and yz multiplied by $e^{-\alpha r^2}$), with orbital exponent of $\alpha = 0.5$. Thus the final Basis Set A may be designated Be(9s4p1d/5s2p1d), while the same notation describes Basis Set B as (9s4p1d/5s3p1d).

All theoretical studies on Be₄ began with self-consistent-field (SCF) wave functions for the ground electronic configuration



At the SCF level of theory, the equilibrium geometry of Be₄ was determined using analytic gradient methods [25] with both basis sets. Harmonic vibrational frequencies were evaluated at the SCF level using analytic second derivative methods [26].

The effects of electron correlation were considered via the method of configuration interaction (CI) [20]. The CI included all single and double excitations, with the restriction that the four core 1s-like molecular orbitals were held doubly occupied in all configurations. Basis Set A only was used for the CI treatment. The Be₄ structure was optimized using analytic CI gradient methods [27] and the harmonic vibrational frequencies were evaluated from finite differences of analytic gradients. To determine the quadratic force constants of Be₄ in internal coordinates, only two gradient calculations are required, both in C_{2v} symmetry. In point group C_{2v} the CI included 7,591 configurations.

RESULTS AND DISCUSSION

Reported in Table 2 are equilibrium geometries, total energies, and harmonic vibrational frequencies for Be₄ predicted at three levels of theory. The bond distances and total energies are consistent with earlier theoretical studies [8-19]. The true Be-Be bond distance is probably 2.07 ± 0.02 Å. This distance is noticeably shorter than the

Be-Be distances in metallic beryllium [28], namely 2.29 Å and 2.23 Å. Another point worth noting is that correlation effects decrease the bond distances in Be_4 , contrary to what is typically found. However, this result may be explained when one appreciates that the lowest unoccupied molecular orbitals (LUMO) of Be_4 are bonding (rather than nonbonding or antibonding, as is usually the case) in nature. Thus double excitations into these bonding orbitals qualitatively strengthen and therefore shorten the six Be-Be bonds.

SCF vibrational frequencies predicted with Basis Sets A and B are in close agreement. The largest difference occurs for the e vibrational mode, for which Basis Set B gives a result 4 cm^{-1} larger than Basis Set A. For this reason only the smaller Basis Set A was used at the CI level of theory.

The predicted CI vibrational frequencies are "nonintuitive" in the sense that two of the three lie above the analogous SCF predictions. For ordinary closed shell molecules, the opposite is usually true. For example, for the set of molecules CH_4 , H_2O , H_2CO , and HCN, the DZ+P CI vibrational frequencies were found [29] to be an average 4.8% lower than the analogous DZ+P SCF predictions. To speculate on whether this result is peculiar to Be_4 or characteristic of other small metal clusters would be premature.

For the sample set of four molecules studied by Yamaguchi and Schaefer [29], the remaining average error in the DZ+P CI harmonic vibrational frequencies was 3.5%. There is of course an additional error relative to the fundamentals due to the neglect of anharmonicity, and for normal closed shell molecules this error is in the same direction [29]. Thus it would not be unreasonable to expect the predicted Be_4 frequencies to be ~ 5% higher than the true frequencies. With this guidance from theory, we would hope to see some intrepid spectroscopic group take up the Be_4 problem in the laboratory, perhaps using infrared matrix isolation techniques.

Herzberg's discussion [30] of the isostructural P_4 molecule shows that for such a tetrahedral molecule, only the triply-degenerate t_2 vibrational mode is infrared active, i.e., both a_1 and e modes are

forbidden in the IR. Using analytic IR intensity methods [31], the t_2 mode is predicted to have intensity (per degenerate component) 0.25 (Basis Set A) and 0.27 (Basis Set B) km/mole. For comparative purposes, this is about the intensity of the O-H symmetric stretching frequency in water. All three fundamental vibrations are Raman-allowed.

As Herzberg notes in his book [30] a molecule with as much symmetry as P_4 (or Be_4) gives rise to a remarkably orderly pattern of vibrational frequencies if the central force approximation (CFA) is adopted. In particular Herzberg shows that in this approximation the vibrational frequencies of a tetrahedral M_4 molecule display the relationship

$$\nu(a_1) : \nu(t_2) : \nu(e) = 2 : \sqrt{2} : 1$$

The theoretical frequencies in Table 2 do not fit this formula well -- a result which is not surprising when one realizes that the CFA amounts to neglecting all off-diagonal elements in the internal coordinate force constant matrix.

ACKNOWLEDGMENTS

We thank Richard B. Remington and Wesley D. Allen for many helpful discussions. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. The Berkeley theoretical chemistry minicomputer is supported by the U.S. National Science Foundation, Grant CHE-8218785.

REFERENCES

1. W. Weltner and R. J. Van Zee, Annual Rev. Phys. Chem. **35**, 291 (1984).
2. M. D. Morse, J. B. Hopkins, P. R. R. Langridge-Smith, and R. E. Smalley, J. Chem. Phys. **79**, 5316 (1983).
3. E. A. Rohlfing, D. M. Cox, A. Kaldor, and K. H. Johnson, J. Chem. Phys. **81**, 3846 (1984).
4. M. E. Geusic, M. D. Morse, and R. E. Smalley, J. Chem. Phys. **82**, 590 (1985).
5. M. B. Wise, D. B. Jacobson, and B. S. Freiser, J. Amer. Chem. Soc. **107**, 1590 (1985).
6. R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor, Phys. Rev. Lett. **54**, 1494 (1985).
7. See, for example, H. F. Schaefer, Accounts Chem. Res. **10**, 287 (1977).
8. C. W. Bauschlicher, D. H. Liskow, C. F. Bender and H. F. Schaefer, J. Chem. Phys. **62**, 4815 (1975).
9. R. B. Brewington, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. **64**, 905 (1976).
10. C. E. Dykstra, H. F. Schaefer, and W. Meyer, J. Chem. Phys. **65**, 5141 (1976).
11. K. D. Jordan and J. Simons, J. Chem. Phys. **67**, 4027 (1977).
12. O. Novaro and W. Kolos, J. Chem. Phys. **67**, 5066 (1977).
13. J. P. Daudey, O. Novaro, W. Kolos, and M. Berrondo, J. Chem. Phys. **71**, 4297 (1979).
14. R. A. Whiteside, R. Krishnan, J. A. Pople, M. Krogh-Jespersen, P. R. Schleyer, and G. Wenke, J. Comput. Chem. **1**, 307 (1980).
15. K. D. Jordan and J. Simons, J. Chem. Phys. **72**, 2889 (1980).
16. H. Stoll, J. Flad, E. Golka, and Th. Krüger, Surface Sci. **106**, 251 (1981).
17. C. W. Bauschlicher, P. S. Bagus, and B. N. Cox, J. Chem. Phys. **77**, 4032 (1982).
18. G. Pacchioni and J. Koutecky, Chem. Phys. **71**, 181 (1982).
19. R. J. Harrison and N. C. Handy, to be published.
20. I. Shavitt, pages 189-275 of Volume 3, Modern Theoretical Chemistry, editor H. F. Schaefer (Plenum, New York, 1977).
21. S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).
22. See, for example, G. A. Somorjai, Chemistry in Two Dimensions: Surfaces (Cornell University Press, Ithaca, 1981); H. Ibach and D. L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations (Academic Press, New York, 1982).
23. F. B. Van Duijneveldt, Research Report RJ945, IBM Research Laboratory, San Jose, California, 1971.
24. D. R. Yarkony and H. F. Schaefer, J. Chem. Phys. **61**, 4921 (1974).
25. P. Pulay, pages 153-185 of Volume 4, Modern Theoretical Chemistry, editor H. F. Schaefer (Plenum, New York, 1977).
26. J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. Symp. **13**, 225 (1979).

27. B. R. Brooks, W. D. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi and H. F. Schaefer, J. Chem. Phys. **72**, 4652 (1980).
28. J. Donohue, The Structures of the Elements (Wiley, New York, 1974).
29. Y. Yamaguchi and H. F. Schaefer, J. Chem. Phys. **73**, 2310 (1980).
30. G. Herzberg, pages 164-165 and 299-300 of Infrared and Raman Spectra (Van Nostrand Reinhold, New York, 1945).
31. Y. Yamaguchi, M. J. Frisch, J. F. Gaw, H. F. Schaefer, and J. S. Binkley, to be published.

Table 1. Be atom basis sets for the theoretical description of Be₄.

Basis Set A: Be(9s4p1d/5s2p1d)

Function Type	Orbital Exponent α	Contraction Coefficient
s	2732.	0.001916
s	410.3	0.014720
s	93.67	0.074290
s	26.59	0.275402
s	8.63	0.720340
s	3.056	1.0
s	1.132	1.0
s	0.1817	1.0
s	0.05917	1.0
p	3.202	0.052912
p	0.6923	0.267659
p	0.2016	0.792085
p	0.06331	1.0
d	0.5	1.0

Basis Set B: Be(9s4p1d/5s3p1d)

Same as Basis Set A except for p function contraction

Function Type	Orbital Exponent α	Contraction Coefficient
p	3.202	0.177439
p	0.6923	0.897586
p	0.2016	1.0
p	0.06331	1.0

Table 2. Structures, total energies, and harmonic vibrational frequencies (in cm^{-1}) for the Be_4 molecule.

		Be[5s2p1d] SCF	Be[5s3p1d] SCF	Be[5s2p1d] CI
Bond distance (Å)		2.083	2.073	2.062
Total energy (hartrees)		-58.35128	-58.35340	-58.52608
Vibrational Frequencies	a_1	651	652	680
	t_2	576	577	589
	e	489	493	487

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*