

Insights into the Structure of Cyclohexane from Femtosecond Degenerate Four-Wave Mixing Spectroscopy and Ab Initio Calculations

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Abstract: In this paper, we report the use of femtosecond time-resolved degenerate four-wave mixing rotationally resolved spectroscopy to obtain very accurate structural information on the symmetric top cyclohexane. Apart from highlighting the versatility of this method in determining accurate structures of large and complex molecules without dipole moment, the present study also details the comparison of the experimentally determined rotational constant B_0 with that obtained from high-level ab initio calculations. The theoretical calculations, which were carried out at both the second-order Møller–Plesset (MP2) and coupled-cluster with single, double, and perturbative triple substitutions [CCSD(T)] levels of theory, also take into account vibrational averaging effects. A detailed investigation of the vibrational averaging effects reveals that the corrections emerge from only the six highly symmetric A_{1g} modes, a justification of which is provided by an analysis of these modes.

Introduction

The evaluation of accurate molecular structures has been one of the most enduring problems in contemporary chemistry.^{1–3} Indeed, it has been said that a detailed understanding of molecular shapes explains virtually all of chemistry.⁴ In this context, high-resolution spectroscopic methods have demonstrated their efficacy in determining the equilibrium geometries of very large polyatomic systems both in the ground and excited states.¹

Despite these dramatic advances, one is still confronted by the odd fact that the equilibrium structure of simple molecules, especially those not possessing a permanent dipole moments, is often obtained by extremely convoluted methods.² Thus cyclohexane (C_6H_{12}), which is one of the smallest saturated cyclic hydrocarbons, has been the focus of a large number of structural investigations because it is totally devoid of ring strain and has no permanent dipole moment.^{6–11,13–16} Both experimental and theoretical investigations concur that the chair

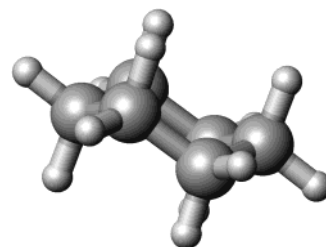


Figure 1. Structure of cyclohexane (chair conformation) obtained after optimization at the CCSD(T)/cc-pVTZ level.

conformer of cyclohexane (Figure 1) is the predominant geometry at room temperature, with the chair conformer being about 8.1 (6.6) kcal/mol more stable than the corresponding boat (or twisted boat) conformation.⁸ Since the pioneering work of Davis and Hassel,⁹ there have been several attempts to obtain the structural characteristics of this chair conformer. The most

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(1) Pratt, D. W. *Annu. Rev. Phys. Chem.* **1998**, *49*, 481.

(2) *Accurate Molecular Structures. Their Determination and Importance*; Domenicano, A., Hargittai, I., Eds.; International Union of Crystallography and Oxford University Press: Oxford, 1992.

(3) Bak, K. L.; Gauss, J.; Jørgensen, P.; Olsen, J.; Helgaker, T.; Stanton, J. F. *J. Chem. Phys.* **2001**, *114*, 6548.

(4) Trindle, C. *Isr. J. Chem.* **1980**, *19*, 47. Wooley, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 1073.

(5) Pauling, L.; Brockway, O. *J. Am. Chem. Soc.* **1937**, *59*, 1223.

(6) Chiu, N. S.; Ewbank, J. D.; Schäfer, L. *J. Mol. Struct. (THEOCHEM)* **1982**, *86*, 397.

(7) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.

(8) Leong, M. K.; Matryukov, V. S.; Boggs, J. E. *J. Phys. Chem. A* **1994**, *98*, 6961.

(9) Davis, M.; Hassel, M. *Acta Chem. Scand.* **1963**, *17*, 1181.

(10) Bastiansen, O.; Fernholt, L.; Seip, H. M.; Kambara, H.; Kuchitsu, H. *J. Mol. Struct.* **1973**, *18*, 163.

(11) Ewbank, J. D.; Kirsch, G.; Schäfer, L. *J. Mol. Struct.* **1976**, *31*, 39.

(12) Hirota, E.; Endo, Y.; Saito, S.; Duncan, J. L. *J. Mol. Spectrosc.* **1981**, *89*, 285.

(13) Alekseev, N. V.; Kitaigorodskii, A. I. *Zh. Strukt. Khim.* **1963**, *4*, 163.

(14) Geise, H. J.; Buys, H. R.; Mijlhoff, F. C. *J. Mol. Struct.* **1971**, *9*, 447.

(15) Peters, R. A.; Walker, W. J.; Weber, A. *J. Raman Spectrosc.* **1973**, *1*, 159.

(16) Shang, Q. A.; Bernstein, E. R. *J. Chem. Phys.* **1994**, *100*, 8625.

recent estimates of the cyclohexane C–C bond length of $1.536 \pm 0.002 \text{ \AA}$ (r_g)¹⁰ and $1.535 \pm 0.002 \text{ \AA}$ (r_g)¹¹ indicate that they are close to the standard value for an unconstrained C–C bond, to be precise, that of ethane ($1.5351 \pm 0.0001 \text{ \AA}$, r_z).¹² However, one should note that all cited distances r_g , r_z are thermally or zero-point averaged ones and, thus, subject to systematic errors larger than the reported statistical ones.

Because cyclohexane in the chair conformation belongs to the point group D_{3d} , it is not possible to employ microwave spectroscopy, the most precise structural method in the gas phase for small- and medium-sized molecules. However several diffractive and spectroscopic methods were employed in the past to obtain information on cyclohexane geometry.^{9–11,13–15} Peters et al. carried out a rotational Raman study and obtained values of the rotational constant $B_0 = 4299.89 \pm 0.06 \text{ MHz}$ (cyclohexane is an oblate symmetric top, where the following relation for the rotational constants holds: $A = B > C$) and the centrifugal distortion constant $D_J = 0.468 \pm 0.009 \text{ kHz}$.¹⁵ Using these values and a simplified r_0 model, the C–C bond length and $H_{eq}CH_{ax}$ angle was found to be $1.535 \pm 0.001 \text{ \AA}$ and $110.0 \pm 0.3^\circ$, respectively.¹⁷ Later, utilizing the fact that unsymmetrically deuterated isotopomers of cyclohexane exhibit a small permanent dipole moment, Dommen et al. determined the precise rotational and centrifugal distortion constants of five isotopomers by Fourier transform microwave spectroscopy and consequently obtained a complete substitution structure (r_s) for cyclohexane.¹⁸ Bialkowska-Jaworska et al. used these results and obtained an improved r_0 structure ($B_0 = 4305.84(15) \text{ MHz}$ and $C_0 = 2463.34(6) \text{ MHz}$) for pure cyclohexane by fitting it to the moments-of-inertia of all five isotopomers of ref 18.¹⁹

The present spectroscopic investigations were undertaken because gas-phase electron diffraction structure determinations are prone to empirical corrections and also to highlight the reliability of our method in obtaining accurate structural information of large molecules possessing no dipole moment.

In the present work, we therefore investigate cyclohexane employing a time-resolved rotational spectroscopic method, namely, femtosecond degenerate four-wave mixing (fs-DFWM), which is a non-linear grating spectroscopy.²⁰ As we have demonstrated in previous contributions, this rotational coherence technique can be employed to study medium-sized molecules, allowing rotational resolution with a relative accuracy of the rotational constants of $\sim 10^{-5}$.^{21–23} Earlier results by fs-DFWM applied to smaller molecules have been reported before by other groups.^{20,24–26} From an investigation of cyclohexane in a gas cell at room temperature as well as in a supersonic jet at very

low-temperature we obtained the precise rotational constant B_0 . We also carried out high-level ab initio calculations of cyclohexane using a large number of basis sets at several levels of theory. In particular, we have evaluated the vibrational averaging effects to critically compare the experimentally determined and theoretically evaluated rotational constants. The contribution of the highly symmetric vibrational modes in this context of vibrational averaging effects is also discussed.

Methods

Experiment and Data Analysis. The experimental setup employed for recording fs-DFWM spectra has been described recently in detail.^{22,23} We used a Ti:sapphire femtosecond chirped-pulse amplified laser system. Its fundamental output radiation (800 nm, 1 kHz, 0.8 mJ/pulse, 200 fs fwhm autocorrelation) is split into two pump beams and one probe beam of identical energy and polarization. The linearly polarized laser beams are overlapped in the sample (gas cell filled with vapor pressure at room temperature or pulsed supersonic expansion) in the so-called forward box arrangement for four-wave mixing, providing the phase matching condition and allowing for the separation of the coherent signal. The fs-DFWM spectrum is recorded as the four-wave mixing signal intensity versus the time delay between pump and probe beams.

For the gas cell experiment the time delay was scanned continuously up to 700 ps in steps of 0.2 ps. Scans around the rotational recurrences (ca. 5 ps wide) with a step size of 0.05 ps have been additionally recorded. For the nonlinear fitting analysis 10 transients in the region up to 700 ps have been considered.

For the supersonic jet experiment the time delay was scanned in two regions (0–350, 1300–1650 ps) with a step size of 0.2 ps. The chosen step size is a compromise between the need to measure the spectra within a short time, so that both regions could be scanned under identical conditions, and the aim of a high accuracy for the rotational constants. For the nonlinear fitting analysis 12 transients have been considered.

The spectral simulation was performed within the framework of a perturbation approach for calculation of the response of the system via the third-order time-dependent polarization. Details are given in refs 23, 27, and 28. For a symmetric top molecule, such as cyclohexane, the experimental fs-DFWM spectrum could be simulated using the following relation:

$$I_{\text{DFWM}}(t) \propto I_{\text{pr}}(t) \otimes (I_{\text{pu}}(t))^2 \otimes \sum_{E_{g'} > E_g} (\rho_{g'} - \rho_g) A_{gg'} \sin(\Omega_{gg'} t)^2 e^{-t/\tau} \quad (1)$$

where $\Omega_{gg'}$ is the fundamental frequency of the Raman transition $g \rightarrow g'$ calculated with respect to the Raman selection rules, $\rho_{g'} - \rho_g$ is the difference in the population (Boltzmann distribution with nuclear spin statistics) of the two levels, $A_{gg'}$ is the orientation integrated Raman transition probability, and τ is an external dephasing time. The result of the sum over all Raman frequencies is convoluted with the temporal evolution $I_{\text{pu}}(t)$ of the pump pulses, squared and convoluted again with $I_{\text{pr}}(t)$, the probe pulse. The laser pulse shapes are assumed to be of Gaussian type.

Recently we have significantly extended the above approach toward the description of general nonrigid asymmetric rotor molecules and applied it successfully for the simulation of the fs-DFWM spectra of pyridine²⁹ and formic acid.³⁰

- (17) For determination of the C–C bond length (r_0) of C_6H_{12} in ref 15 a local C_{2v} symmetry at each carbon atom and a CCC angle of 111.4° was assumed. The C–H bond length was determined from a bond length–bond frequency correlation to 1.102 \AA . It was further assumed that all bond lengths and interbond angles remain the same for the fully deuterated molecule C_6D_{12} .
- (18) Dommen, J.; Brupbacher, Th.; Grassi, G.; Bauder, A. *J. Am. Chem. Soc.* **1990**, *112*, 953.
- (19) Bialkowska-Jaworska, E.; Jaworski, M.; Kisiel, Z. *J. Mol. Struct.* **1995**, *350*, 247.
- (20) Brown, E. J.; Zhang, Q.; Dantus, M. *J. Chem. Phys.* **1999**, *110*, 5772.
- (21) Riehn, C.; Weichert, A.; Brutschy, B. *J. Phys. Chem. A* **2001**, *105*, 5618.
- (22) Riehn, C. *Chem. Phys.* **2002**, *283*, 297.
- (23) Matylytsky, V. V.; Jarzēba, W.; Riehn, C.; Brutschy, B. *J. Raman Spectrosc.* **2002**, *33*, 877.
- (24) Frey, H. M.; Beaud, P.; Gerber, T.; Mischler, B.; Radi, P. P.; Tzannis, A. *P. Appl. Phys. B* **1999**, *68*, 735.
- (25) Lang, T.; Motzkus, M.; Frey, H. M.; Beaud, P. *J. Chem. Phys.* **2001**, *115*, 5418.
- (26) Materny, A.; Chen, T.; Schmitt, M.; Siebert, T.; Vierheilg, A.; Engel, V.; Kiefer, W. *Appl. Phys. B* **2000**, *71*, 299.

- (27) Cho, M.; Du, M.; Scherer, N. F.; Fleming, G. R.; Mukamel, S. *J. Chem. Phys.* **1993**, *94*, 2410.
- (28) Morgen, M.; Price, W.; Ludowise, P.; Chen, Y. *J. Chem. Phys.* **1995**, *102*, 8780.
- (29) Jarzēba, W.; Matylytsky, V. V.; Riehn, C.; Brutschy, B. *Chem. Phys. Lett.* **2003**, *368*, 680.
- (30) Riehn, C.; Matylytsky, V. V.; Gelin, M. F. *J. Raman Spectrosc.* In press.

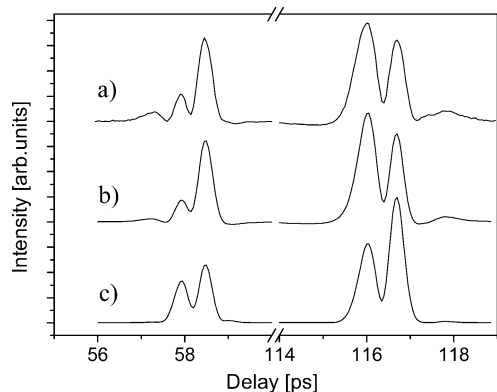


Figure 2. Demonstration of laser intensity dependence for fs-DFWM spectra of cyclohexane. (a) Experimental spectrum from the gas cell (14 mbar, 298 K, 5×10^{12} W/cm²). (b) Fitted simulation, with $k = 0.17$ for reproduction of high laser intensity perturbation. (c) Simulation, with $k = 0$ (low laser intensity). Compare with Figure 3. The explanation for the parameter k is given in the text.

From the described model a fs-DFWM spectrum is calculated with a set of parameters. In particular, we have used as fitting parameters the rotational constant B , the centrifugal distortion constants D_J and D_{JK} , the temperature T , a scaling parameter for the whole spectrum, and an exponential (mainly collisional) coherence decay time τ . A nonlinear fitting routine is automatically varying these model parameters in order to minimize a figure of merit, the reduced χ^2 ; see ref 31. Because the statistical fitting errors obtained from the computer program are usually too optimistic and do not correctly reflect the experimental errors, we have established a grid search error analysis procedure for rotational coherence spectra.^{32,33} Herein the fitting parameters are varied systematically and the 2% boundaries of the minimum of the reduced χ^2 are determined. We report these values as uncertainties σ with a high level of confidence (>95%).

In general, the application of nonlinear optical techniques for molecular spectroscopy has to be performed carefully, obeying the limitations and approximations of the underlying physical model. In the case of fs-DFWM for molecular rotational spectroscopy it was noticed that a change in the shape of the rotational transients occurs with increasing laser intensity.^{23,34} The physical effects behind this spectral change depend on the optical field strength and could range from active alignment³⁵ over molecular deformation³⁶ to field ionization.³⁶

A plain extension of the above simulation procedure works well for an intensity regime in which spectral perturbation just sets in.^{23,29} In this regime a coherently coupled background signal is employed by means of an extra fitting parameter k (0.0 ... 1.0) added to the sum in eq 1 before squaring. In refs 37 and 38 a mixture of homodyne and heterodyne signal detection was calculated in an equivalent way.

In Figure 2 the first two rotational recurrences of cyclohexane are plotted in order to emphasize the change in the transient's modulation

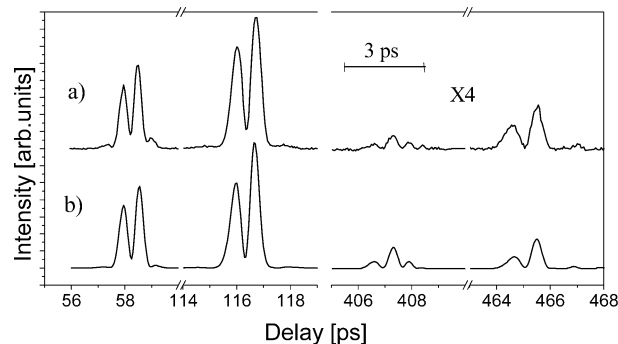


Figure 3. Selected transients from the fs-DFWM spectrum of cyclohexane in the gas cell (25 mbar, 298 K). (a) Experimental spectrum. (b) Fitted simulation (parameters given in Table 1). Please note the different time scales in Figures 3 and 4. A 3 ps ruler is depicted for comparison.

upon increasing laser intensity. Trace (a) in Figure 2 is the experimental spectrum obtained with high laser intensity, trace (b) gives a fitted simulation with, and trace (c) shows a simulation without field-induced perturbation.

The latter trace reproduces very well the experimental spectrum taken under low laser intensity (see also Figure 3a for the corresponding experimental trace). Hence, the two simulations in Figure 2 demonstrate that the spectral perturbation can be accounted for quantitatively, which has been used for the analysis of other molecular systems.^{23,29} In the following we will present and analyze spectra for cyclohexane that were taken at low enough laser intensity so that the extra fitting parameter k was not necessary. However, as Figure 2 also demonstrates, the laser intensity dependence of the fs-DFWM spectra has to be checked carefully for each molecular system.

Cyclohexane (purity 99.5%, ACROS Organics) was studied without further purification. For the cell experiments a typical pressure was 25 mbar. The seeded supersonic expansion was generated from helium as carrier gas (1 bar stagnation pressure) and cyclohexane held at room temperature (vapor pressure ≈ 130 mbar). This gas mixture was expanded into the vacuum by a home-built piezoelectric nozzle (diameter 0.5 mm) operated at 1 kHz repetition rate. The experiment was performed ca. 5 mm downstream from the orifice.

Computational Details. We evaluated the equilibrium structure of cyclohexane (Figure 1) reported in this study using calculations carried out at both the second-order Møller–Plesset (MP2) and the coupled-cluster with single, double, and perturbative triple substitutions [CCSD(T)] levels of theory.^{39–41} Because density functional theory (DFT) predictions of the equilibrium structure are considered to be reliable and are computationally more feasible than the CCSD(T) method, we have also carried out DFT calculations using the hybrid B3LYP functional.^{42,43} A pruned (75,302) grid was used in the B3LYP calculations. This grid contains 75 radial shells, with each shell containing 302 angular points. This results in the evaluation of 7000 points per atom. A large number of basis sets, which include the Dunning's hierarchy of correlation-consistent polarized valence basis sets, cc-pVxZ, aug-cc-pVxZ ($x = D, T, Q$),^{44,45} correlation consistent polarized core-valence basis sets, cc-pCVxZ, aug-cc-pCVxZ ($x = D, T, Q$),⁴⁶ the 6-311++G(3df,2pd) and the TZ2P(f,d) basis augmented with a set of diffuse functions,^{47–50} were employed in the calculations.

- (31) χ^2 is calculated as the squared difference between the experimental and simulated spectrum weighted by assumed uncertainties for each point. Reduced χ^2 and also χ^2_ν are defined by $\chi^2_\nu = \chi^2/\nu$, where ν represents the degrees of freedom given by the number of data points minus the number of parameters to be determined from the data points.
- (32) Riehn, C.; Weichert, A.; Lommatzsch, U.; Brutschy, B. *J. Chem. Phys.* **2000**, *112*, 3650.
- (33) Weichert, A.; Riehn, C.; Barth, H.-D.; Lembach, G.; Zimmermann, M.; Brutschy, B.; Podenas, D. *Rev. Sci. Instrum.* **2001**, *72*, 2697.
- (34) Comstock, M.; Pastirk, I.; Dantus, M. In *Ultrafast Phenomena XII*; Springer-Verlag: Berlin, 2000.
- (35) Péronne, E.; Poulsen, M. D.; Bisgaard, C. Z.; Stapelfeldt, H.; Seideman, T. *Phys. Rev. Lett.* **2003**, *91*, 043003.
- (36) Comstock, M.; Senekerimyan, V.; Dantus, M. *J. Phys. Chem. A* **2003**, *119*, 6546.
- (37) Morgen, M.; Price, W.; Hunziker, L.; Ludowise, P.; Blackwell, M.; Chen, Y. *Chem. Phys. Lett.* **1993**, *209*, 1.
- (38) Lavorel, L.; Faucher, O.; Morgen, M.; Chau, R. *J. Raman Spectrosc.* **2000**, *31*, 77.

- (39) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (40) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (41) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.
- (42) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (43) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (44) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (45) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (46) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *103*, 4572.
- (47) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.
- (48) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
- (49) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

The spherical-harmonic angular functions (5d,7f) were specified when using these basis sets. Thus, the MP2/aug-cc-pVQZ and CCSD(T)/cc-pVTZ calculations of cyclohexane involved geometry optimizations of systems containing 1032 and 348 basis functions, respectively. The corresponding, MP2/cc-pCVQZ and MP2/aug-cc-pCVQZ basis set calculations involved systems containing 864 and 1206 basis functions, respectively. Given the size of the basis set and the number of variables involved, the CCSD(T)/cc-pVTZ calculations represent one of the largest geometry optimizations carried out using the CCSD(T) method. The nuclear gradient convergence criteria for the optimization were that the maximum component of the gradient is less than 4.5×10^{-4} [au], and the root-mean-square (RMS) of the gradient to be less than 3.0×10^{-4} [au]. All electrons (core and valence) were explicitly correlated in the MP2 and CCSD(T) calculations. It has been explicitly pointed out in an earlier study on the accurate determination of molecular equilibrium structures that, in involving the polarized valence cc-pVxZ and aug-cc-pVxZ basis sets, the inclusion of core correlation effects leads to significantly more accurate numbers than those excluding them.³ Both the Gaussian-98 and ACES II programs were used to carry out the geometry optimizations.^{51,52}

Two different approaches have been employed to obtain the magnitudes of the rotational constants at the complete basis set (CBS) limit.^{53,54} It should be mentioned here that these approaches have earlier been employed to estimate the equilibrium bond lengths and harmonic vibrational frequencies at the CBS limit. Thus in the first approach,⁵³ the estimated value of the physical parameter “A” under consideration at the CBS limit can be obtained by employing eq 2:

$$A(X) = A(\infty) + B * \exp[-(X - 1)] + C * \exp[-(X - 1)^2] \quad (2)$$

In eq 2, X is the cardinal number of the basis set (2, 3, 4, for VDZ, VTZ, and VQZ sets, respectively). A(∞) is the estimated CBS limit as $X \rightarrow \infty$. The values of A, B, and C, can be easily obtained, since we have three unknowns and three equations. In a second simpler approach,⁵⁴ the value of “A” at the CBS limit can be obtained by employing eq 3:

$$A(X) = A(\infty) + B * X^{-3} \quad (3)$$

Although it is advantageous to use eq 3 because it involves the evaluation of only two variables and hence requires only two values, we have evaluated the rotational constants at the CBS limit using eq 2, because the mixed exponential/Gaussian function form was often found to yield better agreement with experiment [when $X = 2(\text{VDZ}), 3(\text{VTZ}), 4(\text{VQZ})$] than simple exponential or Gaussian forms.⁵³

- (50) Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 1784.
 (51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, rev. A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.
 (52) Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Tozyczko, P.; Sekino, H.; Huber, C.; Bartlett, R. J. *ACES II; Quantum Theory Project*; University of Florida: Gainesville, FL. Integral packages included are VMOL (Almlöf, J.; Taylor, P. R.); VPROPS (Taylor, P. R.); and ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Taylor, P. R.).
 (53) (a) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484. (b) Petersen, K. A.; Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 7410.
 (54) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

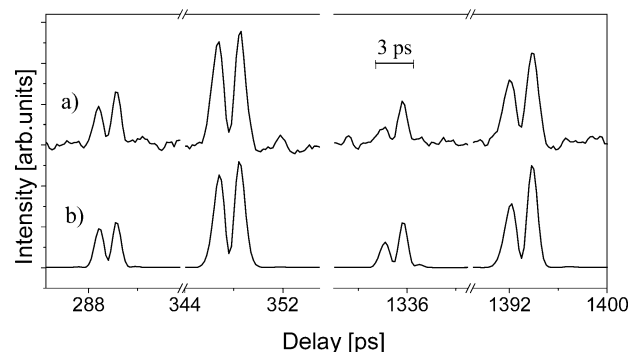


Figure 4. Selected transients from the fs-DFWM spectrum of cyclohexane in the supersonic jet (45 K). (a) Experimental spectrum. (b) Fitted simulation (parameters given in Table 1). Please note the different time scales in Figures 3 and 4. A 3 ps ruler is depicted for comparison.

It is well-known that vibrational anharmonic effects have substantial contributions to the rotational constants.^{3,55–57} Therefore, an effective comparison of the experimentally determined rotational constants to the theoretically evaluated numbers is only feasible when vibrational anharmonic effects are explicitly taken into account while evaluating the latter. Till a few years back, the evaluation of vibrational anharmonic effects was limited to very small molecules because the computationally arduous cubic and quartic force constants⁵⁵ have to be calculated to obtain the magnitude of the vibrational anharmonic effects. However, it has recently been shown that these vibrational anharmonic effects can be easily obtained from only the cubic force constants.^{56,57} Equation 4 represents a mathematical expression for the evaluation of the vibrationally averaged geometries.^{56,57}

$$\langle r_i \rangle = r_{e,i} - \frac{1}{4\omega_i^2} \sum_{j=1}^{3N-6} \frac{V_{ij}^{(3)}}{\omega_j^2} \quad (4)$$

In the above equation, $\langle r_i \rangle$ is the corrected geometry, ω_{ij} are the harmonic frequencies for normal modes i or j , and $V_{ij}^{(3)}$ is the cubic force field. Since the determination of the cubic force constants is a nontrivial task for the size of the systems reported in this study, we have evaluated the vibrational effects at the Hartree–Fock (HF)/6-31G*, HF/cc-pVDZ, and HF/cc-pCVDZ levels. The DALTON program was used to evaluate the vibrational effects.⁵⁸ A detailed analysis of the errors involved in the evaluation of the vibrational effects at both the Hartree–Fock and correlated levels of theory can be obtained from ref 59.

Results and Discussion

In the gas cell the fs-DFWM spectrum was recorded up to 700 ps. Some selected transients are given in Figure 3a in comparison to the fitted simulation (Figure 3b). The fs-DFWM spectrum in the supersonic expansion was measured up to 1.7 ns (Figure 4a) and also compared to a fitted simulation (Figure

- (55) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *123*, 187.
 (56) Åstrand, P.-O.; Ruud, K.; Taylor, P. R. *J. Chem. Phys.* **2000**, *112*, 2655.
 (57) Ruud, K.; Åstrand, P.-O.; Taylor, P. R. *J. Chem. Phys.* **2000**, *112*, 2668.
 (58) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Hättig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Sanchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O. *DALTON*, an electronic structure program, release 1.2; 2001; <http://www.kjemi.uio.no/software/dalton/dalton.html>.
 (59) Pawłowski, F.; Jørgensen, P.; Olsen, J.; Hegelund, F.; Helgaker, T.; Gauss, J.; Bak, K. L.; Stanton, J. F. *J. Chem. Phys.* **2002**, *116*, 6482.

Table 1. Results for fs-DFWM Experiments on Cyclohexane for the Ground State: Rotational Constants and Centrifugal Distortion Constants, Fitting Parameters, Recurrence Times, and Literature Data^a

	fs-DFWM (this work)				
	gas cell	supersonic jet		ref 15	ref 19
	nonlinear fitting	linear regression ^b	nonlinear fitting	rotational Raman	microwave (structural fit)
B [MHz]	4303.22 ± 0.39	4305.14 ± 0.33	4305.44 ± 0.25	4299.89 ± 0.06	4305.85(15)
D_J [kHz]	0.51 ± 0.10		0.51 ^c	0.468 ± 0.009	0.91 ^d
D_{JK} [kHz]	−0.29 ± 0.81		−0.29 ^c		−1.33 ^d
t_j [ps]		58.0699 ± 0.0022			
temp [K]	287 ± 29		45 ± 4	298	220

^a Uncertainties in parentheses are one standard deviation (1 σ). Uncertainties given with $a \pm b$ represent two standard deviations (2 σ). ^b Centrifugal distortion not included. Only peak center positions used. ^c Fixed for the simulation. Values obtained from the gas cell experiment. ^d Δ_J and Δ_{JK} reported. No uncertainties given.

4b) for some selected transients. The fitting results for both the gas cell and the jet data are summarized in Table 1. Also, the results obtained by linear fitting of the supersonic jet data, i.e., by neglect of the centrifugal distortion, are listed.

In comparing the different values from Table 1, one can clearly see that *all* B_0 values obtained from the fs-DFWM experiment are larger than the one formerly reported from Raman spectroscopy by +0.1%.¹⁵ From all three evaluations of the fs-DFWM data, the result from the cell experiment gives the smallest value for this constant.

We have analyzed the gas cell spectrum both with a fixed temperature (298 K) and by using the temperature as a fitting parameter. The results obtained in the latter way are reported in Table 1, since a slightly better reproduction of the spectrum was achieved. However, with a fixed temperature the molecular constants do not change significantly, which can also be seen from the absolute uncertainty of ± 29 K in this case. The relatively high value (45 K) obtained for the temperature in the jet experiment originates from the particular expansion with an enriched gas mixture that did not allow for a strong adiabatic cooling. This expansion condition was indispensable in order to account for the quadratic scaling of the fs-DFWM signal with concentration. The width of the transients depicted in Figures 3 and 4 scales approximately $\sim 1/\sqrt{T}$, which is consistent with general findings on rotational coherence spectroscopy.^{33,60}

The linear regression results of the transient spectrum in the jet gives a value for the rotational constant B_0 that is slightly smaller than that deduced from the nonlinear fitting, since centrifugal distortion is not accounted for. However, this type of analysis is additionally listed here, because it provides a very simple approach toward “relatively” precise rotational constants without complete simulation of the fs-DFWM spectra.

Finally, we recommend the value deduced from the supersonic jet experiment after analysis by nonlinear fitting as new, reliable rotational constant $B_0 = 4305.44(13)$ MHz for cyclohexane. This value is in good agreement with the evaluated constant of ref 19 (see Table 1). The value for B_0 is significantly shifted (+5.5 MHz) from the one reported in the former Raman investigation by Peters et al.¹⁵ Since only room-temperature experiments have been performed in ref 15, the contribution of vibrationally excited levels cannot be ruled out. Moreover, the analysis of the R and S branch gave drastically different rotational and centrifugal distortion constants, so that eventually only the S branch results were reported, a sign for some experimental inconsistency, which was already discussed in ref

15. However, it is difficult to ascertain the source of error. If one considers the B_0 values for C_6D_{12} , a similar shift between the results reported in refs 15 and 19 is noted.

The centrifugal distortion constants, however, determined in this work could only be deduced from the gas cell data and are reported here tentatively and with relatively large error bars (Table 1). Compared to our former investigation on benzene, these larger uncertainties in the case of cyclohexane can be explained by its relatively small anisotropy of the polarizability, which leads to a weak Raman scattering signal. Hence, compared to benzene a higher concentration of cyclohexane in the gas cell was necessary for the measurements, which in turn limits the maximum time window as a result of collisional dephasing (0.7 ns for cyclohexane vs 1.5 ns for benzene). The coherence decay times τ obtained from the fitting were ≈ 130 ps for the gas cell and ≈ 7 ns for the jet experiment. The rotational recurrences at the largest time delay are influenced the strongest by centrifugal distortion, which can be seen from their strong modulation patterns in the case of benzene.²³ For cyclohexane, because of the small maximum time delay, only moderate modulations are found, leading to the large error in the centrifugal distortion constants.

All ab initio calculations were carried out on the chair form of cyclohexane. Because this form possesses D_{3d} symmetry, it can uniquely be described by six geometrical variables. In Table 2, we highlight the variation of some of these variables and the resulting rotational constants of all the optimized structures at the MP2 and CCSD(T) levels. A comparison of these results with those obtained at the B3LYP level can be obtained from the data presented in Supporting Information. While the rotational constants evaluated at the B3LYP level are in better agreement with the experimentally determined numbers, it should be noted that the B3LYP values have not been corrected for vibrational effects. When these corrections are carried out, the calculated B3LYP numbers would be much lower. The use of progressively larger basis sets resulted in an increase of the magnitude of the rotational constants at the MP2 level. This increase in the rotational constants primarily results from a decrease in both the C–C and C–H bond lengths because there are little changes in the magnitudes of the intramolecular angles. Given the size of cyclohexane and the number of variables needed to describe it, it was impossible to carry out the geometry optimizations at the CCSD(T) level using the larger CCSD(T)/cc-pCVTZ and CCSD(T)/cc-pVQZ basis sets. However, the results obtained using the cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ basis sets seem to indicate that the inclusion of higher correlation effects leads to an elongation of the C–C and C–H bond

(60) Felker, P. M.; Zewail, A. H. In *Femtochemistry*; Manz, J., Wöste, L., Eds.; VCH: Weinheim, 1995; Chapter 5, Vol. I.

Table 2. Rotational Constants, Geometries, and Energies of D_{3d} Conformer of Cyclohexane after Geometry Optimization at MP2 and CCSD(T) Levels of Theory and Various Basis Sets^a

MP2						
	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
NBASIS	144	246	348	552	690	1032
<i>A</i> (MHz)	4304.3	4300.3	4391.4	4385.5	4391.4	4389.0
<i>B</i> (MHz)	4304.3	4300.3	4391.4	4385.5	4391.4	4389.0
<i>C</i> (MHz)	2465.6	2465.5	2515.9	2510.8	2514.7	2514.2
R_{C-C}	1.533	1.535	1.520	1.520	1.519	1.520
$R_{C-H_{ax}}$	1.107	1.106	1.091	1.093	1.091	1.092
$R_{C_{Heq}}$	1.104	1.103	1.087	1.090	1.087	1.088
$\theta_{H_{ax}-C-Heq}$	106.7	106.9	106.9	107.0	106.8	106.8
<i>E</i> (hartree)	-235.097937	-235.140311	-235.426092	-235.462115	-235.577647	-235.589667
MP2						
	cc-pCVDZ	aug-cc-pCVDZ	cc-pCVTZ	aug-cc-pCVTZ	cc-pCVOZ	aug-cc-pCVOZ
NBASIS	168	270	426	630	864	1206
<i>A</i> (MHz)	4312.0	4307.6	4372.4	4368.3	4385.7	4383.6
<i>B</i> (MHz)	4312.0	4307.6	4372.4	4368.3	4385.7	4383.6
<i>C</i> (MHz)	2470.6	2470.1	2503.8	2501.6	2511.4	2510.4
R_{C-C}	1.532	1.534	1.523	1.524	1.520	1.521
$R_{C-H_{ax}}$	1.106	1.105	1.093	1.093	1.091	1.092
$R_{C_{Heq}}$	1.103	1.102	1.090	1.090	1.088	1.089
$\theta_{H_{ax}-C-Heq}$	106.8	106.9	106.8	106.9	106.8	106.8
<i>E</i> (hartree)	-235.304651	-235.346824	-235.622287	-235.639145	-235.724640	-235.731412
CCSD(T)						
	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	cc-pCVDZ	aug-cc-pCVDZ	
NBASIS	144	246	348	168	270	
<i>A</i>	4266.0	4256.1	4356.6	4272.9	4263.0	
<i>B</i>	4266.0	4256.1	4356.6	4272.9	4263.0	
<i>C</i>	2441.5	2437.9	2494.0	2446.0	2442.1	
R_{C-C}	1.540	1.543	1.526	1.539	1.541	
$R_{C-H_{ax}}$	1.110	1.109	1.094	1.110	1.109	
$R_{C_{Heq}}$	1.107	1.106	1.090	1.106	1.106	
$\theta_{H_{ax}-C-Heq}$	106.8	107.0	107.0	106.8	106.8	
<i>E</i> (hartree)	-235.203437	-235.248749	-235.535989	-235.423289	-235.457869	

^a NBASIS is the number of basis functions; *A*, *B*, *C*, are the rotational constants; *E* is the energy of the system in hartrees; H_{ax} and H_{eq} are the axial and equatorial hydrogens of cyclohexane. All distances are in units of Å and angles are in degrees.

lengths. Consequently, one observes that the calculated rotational constants are smaller than those obtained at the MP2 level. One can also note that the use of the core-valence basis sets leads to extremely small changes in the geometries and the rotational constants. Because we could not carry out the CCSD(T)/cc-pCVTZ calculation, we believe it is prudent to limit our discussion of the extrapolated results to those involving the valence basis sets. A detailed comparison of the performance of various theoretical methodologies in the elucidation of the equilibrium structures can be obtained from ref 3, wherein the authors have carried out a statistical analysis of the performance of different basis sets at various levels of correlation. It has also been mentioned therein that the use of the valence basis sets with full inclusion of electron correlation, apart from being computationally more feasible, also leads to reliable estimates of the equilibrium geometries.

As was mentioned earlier, we have used the mixed exponential/Gaussian function to estimate the magnitude of these rotational constants at the complete basis set limits.⁵³ Though the above procedure has frequently been employed to estimate the energies of the system at the CBS limit, there has been a report of a similar extrapolation procedure being employed to obtain accurate estimates of the geometries of the ammonium radical.⁶¹ If we use the MP2/cc-pVxZ results, we obtain the values of *B* = 4388.4 MHz and *C* = 2512.1 MHz at the MP2/CBS limit.

The use of the aug-cc-pVxZ values in the extrapolation leads to *B* = 4388.4 and *C* = 2514.9 MHz at the MP2/CBS limit. The presence of only two calculations at the CCSD(T) level prevents us from carrying out a similar extrapolation. However, an estimate of the rotational constants at the CCSD(T)/CBS limit (*B* = 4350.4 MHz and *C* = 2490.3 MHz) was obtained on the assumption that the (CCSD(T)-MP2) difference at the cc-pVQZ level mirrors the difference at the cc-pVTZ level.

Compared to the experimental numbers, the above estimates of the rotational constants are clearly larger by about 80 MHz at the MP2 and about 40 MHz at the CCSD(T) level. This can be rationalized by the fact that results of the calculations are related to the minimum energy structure of cyclohexane and are therefore not corrected for zero-point vibrational effects. Hence, the CBS limit results represent the so-called “global minimum energy structure”, also often referred to as “equilibrium structure”, r_e . Calculations of the vibrational averaging effects require the evaluation of the cubic force constants of cyclohexane, which is computationally not feasible at the correlated levels of theory reported in this study. A number of recent high-level theoretical investigations of small molecules, such as cyclopropane, benzene, and the water dimer, have evaluated the magnitudes of the vibrational corrections for the equilibrium structure rotational constants.^{3,59,62–65} In most cases,

(61) Sattelmeyer, K. W.; Schaefer, H. F.; Stanton, J. F. *J. Chem. Phys.* **2001**, *114*, 9863.

(62) Gauss, J.; Cremer, D.; Stanton, J. F. *J. Phys. Chem. A* **2000**, *104*, 1319.

(63) Gauss, J.; Stanton, J. F. *J. Phys. Chem. A* **2000**, *104*, 2865.

(64) Sinnokrot, M. O.; Sherrill, C. D. *J. Chem. Phys.* **2001**, *115*, 2439.

Table 3. Correction of Calculated Rotational Constants by Vibrational Averaging^a

	uncorrected		corrected		$\Delta(\text{HF})$		$\Delta(\text{MP2})$		$\Delta(\text{CCSD(T)})$	
	6-31G*	cc-pVDZ	6-31G*	cc-pVDZ	6-31G*	cc-pVDZ	cc-pVXZ	aug-cc...	cc-pVTZ	cc-pVXZ
A,B	4319.2	4313.8	4277.2 (4277.2)	4269.8 (4269.7)	42 (42)	44 (44)	83	83	51	45
C	2462.2	2459.9	2437.2 (2434.9)	2433.7 (2431.5)	25 (27)	26.2 (28)	49	52	31	27

^a The corrections are calculated on the HF/6-31G* and HF/cc-pVDZ level of theory. $\Delta(\text{HF})$ denotes the difference between the uncorrected and the corrected rotational constant. $\Delta(\text{MP2})$ and $\Delta[\text{CCSD(T)}]$ denote the difference between the rotational constants of the computational CBS limit and the experimental values. The CBS limit for the CCSD(T) calculations was estimated from the MP2 results (see text). The experimental values used are $B_0 = 4305.44$ MHz from this work and $C_0 = 2463.34$ MHz from ref 18. All values are given in MHz. Values outside of parentheses are for $T = 0$ K; those in parentheses are for $T = 300$ K

the magnitude of this correction is around $\sim 1\%$ of the uncorrected rotational constants.

To provide an estimate for the vibrational averaging effects, we have carried out HF calculations using the 6-31G*, cc-pVDZ, and cc-pCVDZ basis sets using the method delineated in refs 53–56. The results are listed in Table 3. A vibrational correction of ~ 45 MHz for the rotational constant B is obtained, close to the difference between the CBS limit of the CCSD(T) calculations and the experimental values. Also, for the rotational constant C , a vibrational correction of ~ 27 MHz is obtained, which is in close correspondence to the difference of the CCSD(T) calculation, reported here, and the value obtained by fitting the microwave data in ref 18. It has been pointed out previously that the net vibrational averaging effects can be obtained to a fairly good accuracy without the inclusion of electron correlation.^{64,65–68}

Interestingly, of the 48 normal vibrational modes, only the 6 highly symmetric ones (A_{1g}) are responsible for the vibrational averaging effects, which is in line with the conclusions of Salem, who found that only totally symmetric modes contribute to anharmonicity.⁶⁹ To obtain some insight on the origin of these corrections, it is useful to visually examine the vibrational extrema of these 6 symmetric normal modes in Figure 5. Clearly all of them exhibit significantly close atom–atom contacts as a result of displacements from the equilibrium positions. Since by definition the magnitude of the vibration–rotation interaction constants depends on the principal component of the moment of inertia in the equilibrium geometry, the change in the magnitude of the reduced mass would significantly influence the magnitude of anharmonicity.

The calculated temperature dependence of the vibrational correction for the B constant is negligible, whereas in the experiment a shift of approximately 2 MHz was observed (Table 1). This could be explained by the influence of collisions on the gas cell fs-DFWM spectra, which is not accounted for in our simulation model. However, for the rotational constant C , a larger change of 2 MHz was obtained from the calculations. Unfortunately, no experimental values are available for comparison.

In summary, the vibrational correction to the calculated equilibrium rotational constants of cyclohexane provides results that are close to the experimentally determined numbers.

The above theoretical calculations also indicate that reliable estimates of the rotational constants can be obtained by

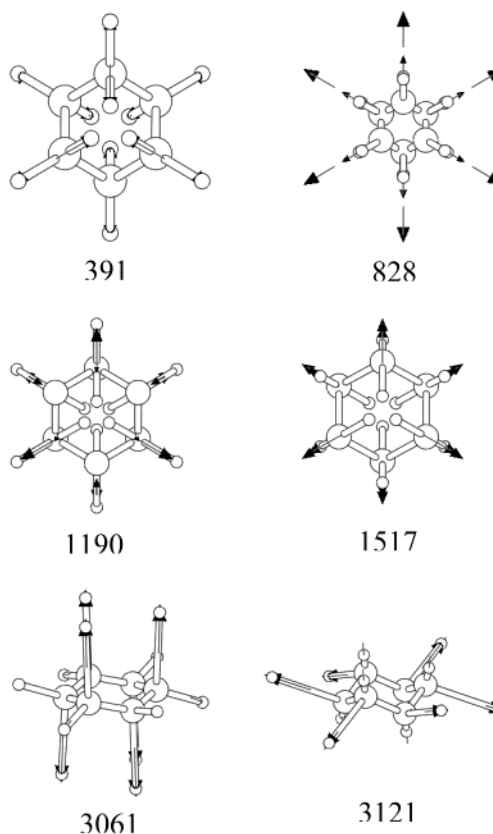


Figure 5. Normal mode plots of the highly symmetric A_{1g} modes of cyclohexane, highlighting the vibrational extrema. The calculated MP2/cc-pCVTZ frequencies (cm^{-1}) of these modes are given below the plots. The normalized displacement vectors shown in the figure have been scaled by a factor of 3.5.

performing geometry optimizations at correlated levels of theory and evaluating the vibrational effects at the HF level.

Conclusions

The rotational constant B_0 of cyclohexane (C_6H_{12}) was re-evaluated from new direct spectroscopic data obtained by femtosecond degenerate four-wave mixing experiments under both gas cell and supersonic jet conditions. The observed shift in B_0 by $+0.13\%$ compared to a former rotational Raman investigation¹⁵ is significant and confirms recent microwave spectroscopic results on deuterated isotopomers of cyclohexane and the subsequently derived r_0 geometry of cyclohexane by structural fitting.^{18,19}

At the complete basis set limit of the ab initio calculations, the estimated rotational constants are shifted toward larger values as compared to the experimental results. This is rationalized as the difference between the minimum energy and the vibrationally averaged structure of cyclohexane. These vibrational

(65) Kim, K. S.; Mhin, B. J.; Choi, U.-S.; Lee, K. *J. Chem. Phys.* **1992**, *97*, 6649.

(66) de Oliveira, G.; Dykstra, C. E. *Theor. Chem. Acc.* **1999**, *101*, 435.

(67) Pulay, P.; Meyer, W.; Boggs, J. E. *J. Chem. Phys.* **1978**, *68*, 5077.

(68) Pulay, P.; Lee, J.-G.; Boggs, J. E. *J. Chem. Phys.* **1983**, *79*, 3382.

(69) Salem, L. *Chem. Phys. Lett.* **1969**, *3*, 99.

corrections primarily emerge from the highly anharmonic symmetric breathing modes of cyclohexane.

The presented results show that fs-DFWM spectroscopy classifies as a precise method for structural analysis in the gas phase. It provides an alternative and innovative approach toward rotational Raman spectroscopy of medium-sized molecules applicable under various experimental conditions. Molecular systems without permanent dipole moment and chromophores can be studied with high precision, and thus molecular benchmark systems for the electronic structure theory are provided. Further systematic improvements of this technique in terms of precision and reliability of the rotational and centrifugal distortion constants for asymmetric top molecules are in progress in our laboratory. First results on the analysis of nonrigid asymmetric top spectra²⁹ and the extraction of information on the polarizability tensor from the fs DFWM spectra³⁰ have been submitted recently.

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Supporting Information Available: Rotational constants, geometries, and energies for cyclohexane obtained from geometry optimization using the density functional (B3LYP), MP2/6-311++G(3df,2pd), and MP2/TZ2P(f,d)+dif methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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