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Electric polarizabilities of $Ge(CH_3)_4$ from collision-induced light-scattering experiments and *ab initio* calculations

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The dipole-quadrupole and dipole-octopole polarizabilities A and E of $Ge(CH_3)_4$ have been determined from collision-induced light-scattering experiments and *ab initio* calculations. Our experimental results are $|A|/e^2a_0^3E_h^{-1}<143$ and $|E|/e^2a_0^4E_h^{-1}<545$. Our best theoretical values are $A=45.48$ and $E=-389.9$, respectively. The calculated value for the dipole polarizability is $\alpha/e^2a_0^2E_h^{-1}=83.26$, in fine accord with our static experimental estimate of 83.2. We present a detailed discussion of the level of agreement between experiment and theory.

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I. INTRODUCTION

Fruitful collaborations between experimentalists and quantum chemists have brought forth significant progress in molecular electro-optics during the past decades. Early work by Buckingham [1] and McLean and Yoshimine [2] provided the theoretical framework for the rigorous definition of electric properties of atoms and molecules. These properties are of fundamental importance to the rational interpretation of wide classes of phenomena, ranging from electron-atom and electron-molecule scattering [3], nonlinear optics [4,5] to various phenomena induced by intermolecular interactions [6,7]. Not all of these properties are easily amenable to experimental measurement [1]. Considerable progress has been made in the rapprochement of theory and experiment in the case of the dipole polarizability (α), first (β), and second (γ) hyperpolarizability [8–10]. Considerably less has been done in the case of dipole-multipole polarizabilities as A (dipole-quadrupole) and E (dipole-octopole). The importance of A and E has been brought forth in systematic investigations in observations on systems of real interest [11]. In systems of tetrahedral or octahedral symmetry the analysis of some classes of spectroscopic observations is dominated by the dipole-quadrupole and dipole-octopole polarizability. In the case of interaction-induced light scattering spectra the work of Bancewicz *et al.* [12] has clearly shown the complementary nature of theoretical and experimental observations. We should also mention here that the work by Hunt and coworkers [13,14] has unambiguously demonstrated that a rigorous treatment of the intermolecular interactions of tetrahedral molecules leans heavily on the availability of accurate values for A and E. It is also worth mentioning that there is renewed interest in the fast, analytical calculation of the dipole-quadrupole polarizability [15]. In recent years, we have reported experimental (P_4 [16], CCl_4 [17], $Sn(CH_3)_4$ [18]), theoretical (CH_4 and CF_4 [19–21], SF_6 [22]), and joint experimental-theoretical [$C_{10}H_{16}$ (adamantane) [23], OsO_4 [24], $TiCl_4$, $ZrCl_4$ and $HfCl_4$ [25]] studies of these properties. Our main goal was to provide reliable values for experimental or theoretical studies but also to test the validity of physical models used in the analysis of experimental observations and, even more, to test the predictive capability of quantum chemical methods and computational strategies in calculations of A and E.

In this project, we have undertaken a systematic study of tetramethyls $M(CH_3)_4$, where $M\equiv C$, Si, Ge, and Sn. First results were obtained in the case of $Sn(CH_3)_4$ [18,26]. In this work, we concentrate on the study of the germanium compound $Ge(CH_3)_4$. Beside the determination of A and E, we also report other important molecular characteristics for this molecule. We also discuss possible effects which make a comparison between experiment and theory for A and E not straightforward.

Atomic units are used throughout this paper. Conversion factors to SI units are as follows: Energy, 1 $E_h=4.359\,748\,2\times10^{-18}$ J, frequency, 1 $E_h/\hbar=4.134\,137\,3\times10^{16}$ s^{-1}, length, 1 $a_0=0.529\,177\,249\times10^{-10}$ m, Ω, 1 $ea_0^3=2.374\,182\times10^{-50}$ C m^3, Φ, 1 $ea_0^4=1.256\,363\times10^{-60}$ C m^4, α, 1 $e^2a_0^2E_h^{-1}=1.648\,778\times10^{-41}$ C^2 m^2 J^{-1}, A, 1 $e^2a_0^3E_h^{-1}=8.724\,958\times10^{-52}$ C^2 m^3 J^{-1}, and E, 1 $e^2a_0^4E_h^{-1}=4.617\,048\times10^{-62}$ C^2 m^4 J^{-1}. Property values are mostly reported as pure numbers, that is Ω/ea_0^3, Φ/ea_0^4, $\alpha/e^2a_0^2E_h^{-1}$, $A/e^2a_0^3E_h^{-1}$, and $E/e^2a_0^4E_h^{-1}$.

II. EXPERIMENTS

The dipole-multipole polarizabilities A and E are obtained from gas-phase depolarized collision-induced light scattering (CILS) experiments. The experimental procedure as well as the analysis of the recorded spectra have been described in detail before [17,18] and are repeated here only briefly.

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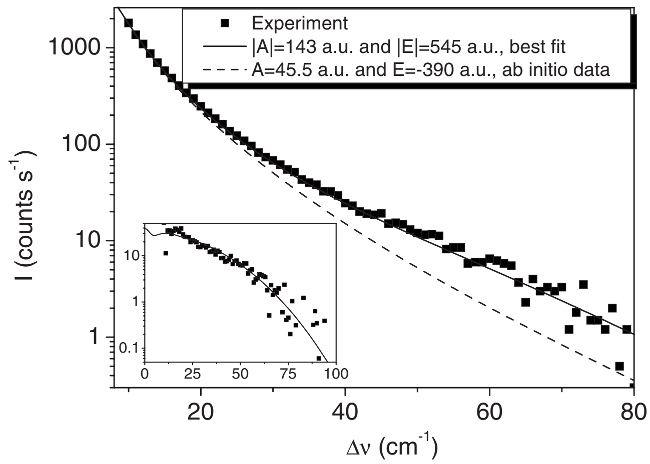


FIG. 1. Depolarized CILS spectrum of gaseous $Ge(CH_3)_4$ (experiment: full squares; best fit to experimental spectrum: full line; simulated spectrum with *ab initio* results of A and E: dashed line). The experimental conditions are $\omega=0.0886E_h/\hbar$, $T=458.0$ K, $p_V=23.76$ bar and density $\rho=800.9$ mol m^{-3}. The squares in the inset show the difference between the experimental and simulated spectrum; the full line in the inset gives the approximate line shape of a spectrum produced by double rotational transitions.

The light scattering experiments are carried out in the usual 90° scattering geometry. The laser light source delivers 1 W at 514.5 nm ($\omega=0.0886E_h/\hbar$). The light is focused into a cylindrical scattering cell. After passing a Coderg T800 triple monochromator the scattered intensity is recorded with a photomultiplier tube cooled down to -20 °C. A photon counting technique is employed. The scattering cells are small glass tubes with inner diameter of 4 mm and height of 10 cm. The cells are filled with a small amount of liquid $Ge(CH_3)_4$, which has a purity of better than 99.9%. The $Ge(CH_3)_4$ was frozen with liquid nitrogen, evacuated down to a pressure of <0.1 Pa and melted off. The so prepared sample cells are placed inside a massive cylindrical stainless steel sample holder which serves as a thermostat. The sample holder is heated with a heating ribbon. The temperature is recorded with NiCr-Ni thermocouples. The most successful experiments were carried out at $T=458$ K. Above this temperature decomposition of the sample was observed. From the experimentally known vapor pressure $p(T)$ [27,28] and the calculated second virial coefficient $B(T)$ (see below), the density ϱ of the $Ge(CH_3)_4$ vapor is calculated according to $\varrho=\varrho_0[1-B(T)\varrho_0]$, with $\varrho_0=p/(RT)$. In our studies the density range is 500–800.9 mol m^{-3}.

The collision-induced light scattering spectrum is recorded in the range between 10 and 100 cm^{-1} with a resolution of about 2.0 cm^{-1}. As in our latest study on $Sn(CH_3)_4$ [18], the anti-Stokes part of the collision-induced spectrum is used for analysis. A typical CILS spectrum of gas-phase $Ge(CH_3)_4$ is shown in Fig. 1.

Similar to our previous work [16,24,25], the CILS spectra are analyzed via a procedure described by Posch [29]. We rely on the point-multipole approximation of the contributions to the depolarized interaction-induced light scattering spectra. These contributions can be split into several distinct parts. First we separate the contributions of bound and metastable dimers. Their contributions are concentrated in the vicinity of the Rayleigh line. The major part of the interaction induced spectra results from contributions of collisional complexes. In the case of tetrahedral molecules, the CILS intensity can be split into a pure translational spectrum and a collision-induced rotational Raman (CIRR) spectrum [30]. The point multipole expansion of the incremental pair polarizability yields

$$\langle\alpha^{(2)}(0)\odot\alpha^{(2)}(t)\rangle F^{(2)}_{\mathrm{DID}}(t)+F^{(2)}_{\mathrm{DQ}}(t)+F^{(2)}_{\mathrm{DO}}(t)+F^{(2)}_{\mathrm{QQ}}(t)+\cdots, \tag{1}$$

where the subscripts refer to dipole-induced-dipole, dipole-quadrupole, dipole-octopole, and quadrupole-quadrupole contributions, respectively. In the case of the incremental pair-polarizability anisotropy which enters in $F^{(2)}_{\mathrm{DID}}(t)$, the usual approximation,

$$\Delta\alpha(\omega,R)=6\alpha^2(\omega)R^{-3}+\left(6\alpha^3(\omega)+\frac{\gamma C_6}{3\alpha(\omega)}\right)R^{-6}+B\exp(-R/R_0), \tag{2}$$

is used, where $\alpha(\omega)$ is the polarizability of an isolated molecule at the measuring frequency ω, γ is the second hyperpolarizability, and C_6 is the constant of the R^{-6} term in the dispersion-interaction energy. In our case, C_6 and γ are not known. Hence we use the approximation [31]

$$\left(6\alpha^3(\omega)+\frac{\gamma C_6}{3\alpha(\omega)}\right)\approx 6\alpha(\omega)[\alpha^2(\omega)+1.14S(-4)], \tag{3}$$

where $S(-4)$ is the second term in the Cauchy expansion of the frequency dependence of the mean dipole polarizability $\alpha(\omega)=\Sigma_k S(-2k)\omega^{2k-2}$.

The other parts in Eq. (1) are given by [29]

$$F^{(2)}_{\mathrm{DQ}}=A^2(\omega)\alpha^2(\omega)\frac{768\pi}{49}\langle S_3(t)R_3(t)\rangle, \tag{4}$$

$$F^{(2)}_{\mathrm{DO}}=E^2(\omega)\alpha^2(\omega)\frac{880\pi}{81}\langle S_4(t)R_4(t)\rangle, \tag{5}$$

$$F^{(2)}_{\mathrm{QQ}}=A^4(\omega)\frac{125\,824\pi}{945}\langle S_3(t)R_4(t)\rangle. \tag{6}$$

$A(\omega)$ and $E(\omega)$ are the dipole-quadrupole and dipole-octopole polarizabilities at measuring frequency ω. In the case of T_d symmetry, they can be represented by a single scalar quantity. $\langle S_\ell(t)\rangle$ are the rank ℓ tensor correlation functions and $R_\ell(t)$ is the Fourier transform of the free-rotor spectral density $R_\ell(\omega)$. More details and the explicit formulation of $S_\ell(t)$ and $R_\ell(t)$ are given by Posch [29,32,33].

The aim of our analysis is to obtain values of A and E, and the short-range parameters B and R_0, Eq. (2). As known input parameters we use the rotational constant $B_{\mathrm{rot}}=0.094\,638$ cm^{-1} [34] and the Lennard-Jones (12-6) potential parameters $\varepsilon/k=328$ K and $\sigma=6.236\times10^{-10}$ m [35], k being the Boltzmann constant. The dynamic dipole-polarizability of $\alpha(\omega)=88.2$ $e^2a_0^2E_h^{-1}$ at our measuring frequency of 514.5 nm is obtained from a suitable combination of two experimental liquid phase data [36,37]. These data also provide a reliable estimate of the static dipole polarizability $\alpha(0)=83.2\ e^2a_0^2E_h^{-1}$, very close to our theoretical findings (see below). From these data we also obtain the estimate $S(-4)=627$ a.u. (for details, see [18]).

III. EXPERIMENTAL RESULTS

The best fit to our experimental spectrum is shown in Fig. 1. First it is interesting to note that the Lennard-Lones (12-6) potential parameters of $\varepsilon=328$ K and $\sigma=6.236\times10^{-10}$ m [35], which are obtained from critical properties, are able to reproduce the measured CILS spectrum. It is well known that the calculated line shape is very sensitive to a variation of the potential parameters and always gives a good indication for the suitability of the underlying intermolecular-interaction energy model [38,39]. We have limited the useful spectral range to $10\leq\Delta\nu/\mathrm{cm}^{-1}\leq80$ because of the relatively poor signal-to-noise ratio at higher wave number shifts. From the experiments upper limits of the dipole-quadrupole and dipole-octopole polarizabilities are obtained as $|A(\omega)|=(143\pm10)\ e^2a_0^3E_h^{-1}$ and $|E(\omega)|=(545\pm220)\ e^2a_0^4E_h^{-1}$, We also notice that the exponential short-range term $B\exp(-R/R_0)$ in Eq. (2) gives a measurable contribution to the DID term of the collision-induced polarizability anisotropy. We find $B=(25\,500\pm4000)\ e^2a_0^2E_h^{-1}$ and $R_0=0.667\times10^{-10}$ m. The result $B>0$ is contrary to previous findings where in most cases $B<0$ is observed [16,18,25,40].

IV. QUANTUM CHEMICAL STUDY

A. General considerations

Our approach to the calculation of the electric properties leans on the finite-field method [41]. The energy (E^p), dipole (μ^p_α), quadrupole ($\Theta^p_{\alpha\beta}$), and octopole ($\Omega^p_{\alpha\beta\gamma}$) moment interacting with a weak, static homogeneous field can be written as [1,2]

$$\begin{aligned}E^p = E^0 &- \boldsymbol{\mu}_\alpha F_\alpha - 1/3\boldsymbol{\Theta}_{\alpha\beta}F_{\alpha\beta} - 1/15\boldsymbol{\Omega}_{\alpha\beta\gamma}F_{\alpha\beta\gamma}\\ &- 1/105\boldsymbol{\Phi}_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta} + \cdots - 1/2\boldsymbol{\alpha}_{\alpha\beta}F_\alpha F_\beta\\ &- 1/3\mathbf{A}_{\alpha,\beta\gamma}F_\alpha F_{\beta\gamma} - 1/6\mathbf{C}_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta}\\ &- 1/15E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta} + \cdots - 1/6\boldsymbol{\beta}_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma\\ &- 1/6\mathbf{B}_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta} + \cdots - 1/24\boldsymbol{\gamma}_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \cdots,\end{aligned} \tag{7}$$

$$\mu^p_\alpha = \boldsymbol{\mu}_\alpha + \boldsymbol{\alpha}_{\alpha\beta}F_\beta + 1/2\boldsymbol{\beta}_{\alpha\beta\gamma}F_\beta F_\gamma + 1/6\boldsymbol{\gamma}_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \cdots, \tag{8}$$

$$\Theta^p_{\alpha\beta} = \boldsymbol{\Theta}_{\alpha\beta} + \mathbf{A}_{\gamma,\alpha\beta}F_\gamma + 1/2\mathbf{B}_{\gamma\delta,\alpha\beta}F_\gamma F_\delta + \cdots, \tag{9}$$

$$\Omega^p_{\alpha\beta\gamma} = \boldsymbol{\Omega}_{\alpha\beta\gamma} + \mathbf{E}_{\delta,\alpha\beta\gamma}F_\delta + \cdots, \tag{10}$$

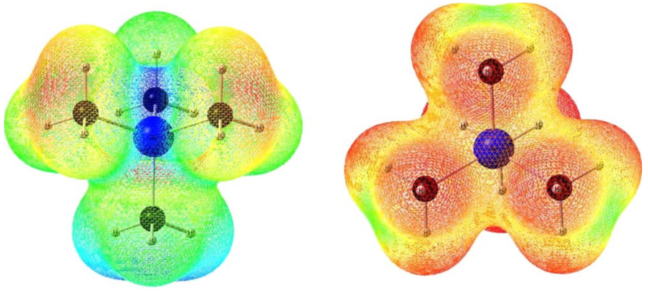
where $F_a,\ldots$ is the field at the origin. The terms in bold are permanent properties of the perturbed system. E^0, μ_α, $\Theta_{\alpha\beta}$, and $\Omega_{\alpha\beta\gamma}$ are the energy and permanent multipole moments of the free molecule. $\alpha_{\alpha\beta}$ is the dipole polarizability and $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ the hyperpolarizabilities. $A_{\alpha,\beta\gamma}$ and $E_{\alpha,\beta\gamma\delta}$ are the dipole-quadrupole and dipole-octopole polarizability, respectively. $B_{\alpha\beta,\gamma\delta}$ is the dipole-dipole-quadrupole hyperpolarizability. A repeated subscript implies summation over x, y, and z. We adopt the standard orientation for a tetrahedral molecule as $M\mathrm{Cl4}_4$ with the M atom at the origin (0,0,0) and the M-Cl bonds on the directions defined by the origin and (1,1,1), (1,−1,−1), (−1,1,−1), and (−1,−1,1). There is only one independent component of the octopole ($\boldsymbol{\Omega}_{\alpha\beta\gamma}$) and hexadecapole ($\boldsymbol{\Phi}_{\alpha\beta\gamma\delta}$) moment or the dipole ($\boldsymbol{\alpha}_{\alpha\beta}$), dipole-quadrupole ($\mathbf{A}_{\alpha,\beta\gamma}$), and dipole-octopole ($\mathbf{E}_{\alpha,\beta\gamma\delta}$) polarizability [1,42]. As the dipole-quadrupole and dipole-octopole are the properties of interest in this work, we simplify notation hereafter and denote them as A and E. As a by-product of our effort, we also calculate the octopole and hexadecapole moment, hereafter Ω and Φ.

A full presentation of our computational approach to the molecular properties of interest in this work may be found in previous work [19–21,23–25]. The theoretical methods employed here are the conventional *ab initio* SCF (self-consistent field) and MP2 (second-order Moeller-Plesset perturbation theory) and the widely used Becke three-parameter Lee-Yang-Parr (B3LYP) density-functional theory method [43].

B. Computational details

The selection of suitable basis sets of Gaussian-type functions (GTF) constitutes an essential part of molecular property calculations [44]. Although systematic work on the construction of basis sets for electric polarizability is known [45], little is known for the case of the dipole-multipole polarizabilities as A and E. We lean heavily on previous experience on dipole and quadrupole (hyper)polarizability calculations [46–48] and especially on our previous work on the calculation of A and E for tetrahedral systems [19–21,23–25] in order to design suitable basis sets for $Ge(CH_3)_4$. We selected for Ge/C/H a substrate consisting of $(14s10p5d)/[5s4p2d]$ for Ge [49] and $(9s5p/4s)[4s2p/2s]$ for C/H [50]. Following a computational philosophy expanded in detail in previous work [46], the initial substrate was augmented with diffuse s- and p-GTF on Ge/C and s-GTF on H. In a further step, we added one d-GTF on C and one p-GTF on H with exponents chosen to minimize the energy of the free molecule. The construction was completed with the addition of one d-GTF on Ge/C and one p-GTF on H with exponents chosen to maximize the dipole polarizability. The resulting basis, hereafter B1, is of $[6s5p3d/5s3p2d/3s2p]$ size and consists of 240 contracted GTF. We used two even larger basis sets: B2 $=[6s5p4d1f/5s3p3d/3s3p]$ consisting of 308 CGTF and B3$=[6s5p4d1f/5s3p3d1f/3s3p1d]$ or 396 GTF. 5D and 7F were used in all cases.

All optimizations and subsequent calculations were performed at the MP2 (full)/cc-pVDZ (correlation-consistent polarization valence double zeta) molecular geometry with the Gaussian 98 program [51].



HOMO LUMO

FIG. 2. (Color online) Total SCF density in $Ge(CH_3)_4$ mapped with the HOMO and LUMO.

C. Basic molecular characteristics

All molecular properties calculated in this work pertain to the MP2 (full)/cc-pVDZ geometry. The relevant geometrical parameters are, in Å and deg, $R(\text{Ge-C})=1.960\,996$, $R(\text{C-H})=1.102\,356$, $\measuredangle(\text{Ge-C-H})=110.7899$, and $\measuredangle(\text{H-C-H})=108.1210$. Relying on a MP2 calculation with the $B1=[6s5p3d/5s3p2d/3s2p]$ basis set, we have determined atomic charges via a natural bond orbital (NBO) population analysis. We obtain +1.591 27 (Ge), −1.032 35 (C), and +0.211 51 (H). In Fig. 2 we show the total SCF density mapped with the HOMO and LUMO.

D. Theoretical results

Our calculated values for Ω, Φ, α, A, and E are shown in Table I. We expect our large B3 basis set to provide reference values for all levels of theory. At the SCF/B3 level we obtain the following values: $\Omega=-24.15$, $\Phi=20.36$, $\alpha=78.22$, $A=32.65$, and $E=-345.0$. These values should be of near-Hartree-Fock quality. It is worth noticing that the multipole moments show clearly stronger basis set dependence than the polarizabilities. In absolute terms, B1 yields SCF values for Ω, Φ, α, and A 2.8, 12.2, 0.2, and 0.7% lower than the reference SCF/B3 value. The SCF/B1 value of E is 1.6% above the SCF/B3 result.

The MP2-B3 values are $\Omega=-23.15$, $\Phi=18.48$, $\alpha=83.26$, $A=45.48$, and $E=-389.9$. Electron correlation reduces the magnitude of the multipole moment values. The opposite is observed for the polarizabilities. The magnitude of the MP2/B3 values for α, A, and E is 6.4, 39.3, and 13.0% above the SCF/B3. We observe that the B3LYP values are fairly close to the MP2 *ab initio* results. As expected from previous experience [25], the B3LYP-B3 values are larger than the respective MP2-B3 values.

E. Recommended theoretical values and comparison with experiment

We have obtained an experimental estimate (see above) for the dipole polarizability $\alpha=83.2$, very close to our MP2-B3 value of 83.26. We consider this a very encouraging sign for the general state of things in this joint experimental-theoretical study.

Based on our values and experience from previous work on similar systems, we advance the following theoretical estimates for the dipole-quadrupole and dipole-octopole polarizability: $A=45.5\pm4.5$ and $E=-(390.0\pm78.0)$. The theoretical value of A is well below the experimentally obtained upper limit of 143. We find a better agreement for $|E|$, where the theoretical value lies well within the limits of the experimental uncertainty.

V. DISCUSSION AND CONCLUSIONS

Our combined experimental and theoretical study on the dipole-polarizabilities of $Ge(CH_3)_4$ has revealed a striking discrepancy between the experimentally obtained and purely calculated depolarized collision-induced light scattering spectrum. Similar mismatches for molecules of T_d symmetry were also found before in the case of CF_4 [52], $C(CH_3)_4$ [29], and $Sn(CH_3)_4$ [18,26], where in each case the scattering

TABLE I. Theoretical values and experimental estimates for the electric properties of $Ge(CH_3)_4$.

Approach	Method	Basis set[a]	Ω	Φ	α	A	E
Theory	SCF	B1	−23.50	17.87	78.10	32.43	−350.5
		B2	−24.17	21.48	78.18	32.54	−346.9
		B3	−24.15	20.36	78.22	32.65	−345.0
	MP2[b]	B1	−22.80	20.74	82.72	43.72	−393.7
		B2	−23.06	21.58	83.11	45.01	−393.1
		B3	−23.15	18.48	83.26	45.48	−389.9
	B3LYP	B1	−21.40	18.05	84.42	46.57	−405.7
		B2	−21.90	21.98	84.71	46.66	−407.6
		B3	−21.80	17.59	84.70	46.75	−405.1
Experiment[c]					83.2[d]	<143	<545

[a] $B1=[6s5p3d/5s3p2d/3s2p]$, $B2=[6s5p4d1f/5s3p3d/3s3p]$, and $B3=[6s5p4d1f/5s3p3d1f/3s3p1d]$.

[b] The thirteen innermost MO were kept frozen in the MP2 calculations.

[c] Absolute values are given for A and E; see text.

[d] Static experimental estimate; see text.

intensity calculated with the theoretical results for A and E is less than the experimental one. We will discuss possible effects for this observation. In the case of $Ge(CH_3)_4$, our experimental results pertain to a wavelength of 514.5 nm and a temperature of 458 K, whereas the calculations are carried out at zero frequency and temperature. There is theoretical evidence that the effects of frequency dispersion and excitation of vibrational and rotational modes increase the dipole-multipole polarizabilities [15]. However, this increase might not exceed 5% in our case which could not explain the observed discrepancy in A.

Another reason for the observed discrepancy is the truncation of the power series in Eq. (1) after the quadrupole-quadrupole term $F_{QQ}^{(2)}(t)$. Higher-order linear terms and the complete set of nonlinear contributions to the rototranslational spectrum were ignored at our level of approximation. In the case of CF_4, Elliasmine *et al.* have shown that nonlinear terms have only a minor effect on the individual contributions to the collision-induced spectrum [52]. Also higher-order linear terms produced by coupling of A and E or E and E are found to have only small effects in the spectral range we are interested in. Due to its complexity at this point, we have no other choice than to assume the same behavior for the $Ge(CH_3)_4$ molecule.

The long-range parts of the series expansion, Eq. (2), are obtained via a multipole expansion and have been extended to higher order terms [12]. The short-range term $B\exp(-R/R_0)$, however, accounts for a number of different effects, such as overlap, exchange, and orientational contributions. It is, therefore, very approximate in nature. In fitting the chosen model, Eq. (2), to the experimentally recorded CILS spectrum, neglected terms might show up also in the parameters B and R_0. Therefore, an interpretation of these two parameters for such a large molecule as $Ge(CH_3)_4$ is not straightforward and perhaps not possible at all.

Another crucial point in evaluating CILS spectra concerns the intermolecular-interaction potential U. It is well known that the calculated trajectories of the molecules and therefore the line shapes and intensities are strongly effected by the choice of U. In our case there is only one intermolecular-interaction potential function available, which is given in the form of a simple Lennard-Jones (12-6) potential [35]. This potential is deduced from critical properties. At 298.15 K and 273.15 K it yields for the second pVT-virial coefficient $B(T)$ $-915\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ and $-1064\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$, whereas the experimental estimates are $-1400\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ (298.15 K) [53] and $-2800\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ (273.15 K) [54], respectively. Due to the approximate nature of these two experimental results, it is not possible to give a final judgment about the quality of the potential energy function used.

In our discussion, we have concentrated so far on the undistorted molecule. A possible frame-distortion effect has not been taken into account. One can assume that a collision between molecules will lead to a change in bond angles and bond lengths, giving rise to additional terms in the pair-polarizability tensor [55] and the collision-induced dipole moment [56,57]. Shelton and Tabisz [55] have given an approximate formula to account for this effect in CILS spectra. We have calculated the induced anisotropy $\Delta\alpha$ of the polarizability tensor of $Ge(CH_3)_4$ by changing the length R of a single Ge-C bond. At the SCF-B1 level we found $d\Delta\alpha(R)/dR = 18.9 e^2 a_0 E_h^{-1}$. As already argued by Shelton and Tabisz [55], this positive value decreases the calculated scattered intensity. Invoking this effect into our line-shape calculations results in a 6% increase in the experimentally observed A tensor, if we do not relax the other properties (E, B, R_0) in our fitting procedure. This shows that frame distortion has an observable effect in collision-induced light scattering experiments. Its effect should increase with an increasing number of internal degrees of freedom of the molecule.

We would like to stress another effect caused by frame distortion. In our case, we have shown by *ab initio* calculations that variation of a single Ge-C bond length leads to a reduction to C_{3v} symmetry and an induced polarizability anisotropy $\Delta\alpha \neq 0$. This induced anisotropy gives rise to a rotational Raman spectrum which in the simplest case would be that of a symmetric top molecule [58]. Since it is caused by two now anisotropic interacting molecules, we can assume an underlying double rotational transition. Double transitions are known to occur even for the undistorted molecule in the nonlinear contributions to the rototranslational spectrum [12] as well as in the linear $F_{QQ}^{(2)}(t)$ term in Eq. (1) [30]. By using the rotational constant B_{rot}, we have deduced an approximate line shape of this contribution. We did not attempt to calculate the corresponding absolute scattering intensity of this collision-induced double rotational transition. Even in the case of molecular hydrogen the treatment of this phenomenon is by no means simple and would be a special subject on its own [59]. In the inset of Fig. 1 the shape of this spectrum is compared to the difference between the experimental CILS spectrum and its simulated analog. The similar behavior is striking. It might give a hint that the neglect of double transitions of the frame distorted molecules leads to the observed discrepancies.

In an overall evaluation of our present effort, we stress the fact that we have succeeded in producing a reliable estimate of the static polarizability α of $Ge(CH_3)_4$, a property of universal importance in molecular science. Furthermore, we have observed a discrepancy between theory and experiment for the dipole-quadrupole but an essential agreement for the dipole-octopole polarizability. The completion of our project on the sequence of tetramethyls $C(CH_3)_4$, $Si(CH_3)_4$, $Ge(CH_3)_4$, and $Sn(CH_3)_4$ and the critical analysis of previous findings by other authors will put us in a position to advance more far-reaching conclusions on the validity of our approach.

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