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# *Ab initio* study of third-order nonlinear optical properties of the $H_2$ and $D_2$ molecules

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Third-order dynamic hyperpolarizabilities ($\gamma$) for $H_2$ and $D_2$ are calculated using James-Coolidge-type wave functions for several internuclear distances and frequencies. From them, third-order susceptibilities ($\chi$) relevant to dc Kerr, degenerate four-wave mixing, electric-field-induced second-harmonic generation and third-harmonic generation experiments are determined. Agreement with the electric-field-induced second-harmonic generation experimental data is very good: $\chi_{\parallel}^{(3)}=792$, 821, and 959 a.u. for $\lambda=6943$, 6328, and 4880 Å, compared with the experimental values: 805, 828, and 973 a.u. Other aspects such as dispersion formulas, Kleinman symmetry, and vibrational contributions are also investigated and discussed.

## I. INTRODUCTION

Since the discovery of optical second-harmonic generation in 1961,[1] a new and exciting field of quantum electronics has developed and, with the invention of different types of powerful and tunable lasers, many nonlinear optical processes have been found. Useful reviews, from both theoretical and experimental viewpoints, have been written by Franken and Ward,[2] Orr and Ward,[3] Bogaard and Orr,[4] Shen,[5] and Bloembergen.[6] The processes we are concerned with here are analogous to that responsible for refractive index, that is to say, a coherent scattering effect which arises from the interaction of an intense electric field from a laser beam with the nonlinear microscopic hyperpolarizabilities of the material under observation. In particular, we consider the dc Kerr effect, degenerate four-wave mixing or nonlinear intensity-dependent refractive index (DFWM), electric-field-induced second-harmonic generation (ESHG), and third-harmonic generation (THG). The equally important phenomenon of coherent anti-Stokes Raman spectroscopy (CARS) will not be discussed.

All these processes can be defined by the general equation[4,7]

$$P_i(\omega_\sigma)=K\bar{\chi}^{(3)}_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)\ , \qquad (1)$$

where $i,j,k,l$ are laboratory-frame axes, $E_j(\omega)$ is the $j$th component of the applied field oscillating with a frequency $\omega$, $P_i(\omega_\sigma)$ is the induced macroscopic polarization oscillating at $\omega_\sigma(\omega_\sigma=\omega_1+\omega_2+\omega_3)$. $K$ is a numerical factor, and $\bar{\chi}^{(3)}_{ijkl}$ is the temperature-dependent third-order macroscopic susceptibility.

We report accurate calculations of the parallel components $\bar{\chi}^{(3)}_{ZZZZ}=\bar{\chi}^{(3)}_{\parallel}$ (at $T=22\,^{\circ}\mathrm{C}$) for the hydrogen molecule (and its isotope $D_2$) for the following: $\bar{\chi}^{(3)}_{\parallel}(-\omega;0,0,\omega)$, one component of dc Kerr; $\bar{\chi}^{(3)}_{\parallel}(-\omega;\omega,\omega,-\omega)$, DFWM; $\bar{\chi}^{(3)}_{\parallel}(-2\omega;0,\omega,\omega)$, ESHG; and $\bar{\chi}^{(3)}_{\parallel}(-3\omega;\omega,\omega,\omega)$, THG. Values will be given for the static case ($\omega=0$) and for three frequencies which correspond to the experimentally accessible wavelengths of 4880 Å (argon-ion laser), 6328 Å (He-Ne laser), and 6943 Å (ruby laser). Contributions which result from the displacement of the nuclei by the applied fields will also be separately and explicitly evaluated (the so-called "vibrational" terms).[7-9]

Though the theory of these processes has been in place for some time, there has so far been very little numerical exploitation for molecules. Exceptions for the hydrogen molecule are the work of Watts and Stelbovics[10] (ESHG at 6943 Å), Jaszuński and Roos[11] (DFWM and THG for a range of frequencies), and Huo and Jaffe[12] (CARS). However, all these efforts are, as will be described after we have given our own results, in one way or another limited. This dearth of accurate theoretical values is the more surprising since the experimental values are most commonly found relative to those of another species: hence the need for a "benchmark" value, for, say, $H_2$, if absolute values are to be known. To date, the 1968 calculation of Sitz and Yaris[13] on He has had to serve this purpose: a calculation which gives a static result for $\alpha$ which lies outside the rigorous bounds given by Glover and Weinhold.[14]

Recently, Mizrahi and Shelton[15] have determined ESHG results for $H_2$ to an accuracy much greater than previous experiments and they detect a discrepancy between published theoretical static values and their own results extrapolated to $\omega=0$. We wish to investigate this problem, as well as to compare *directly* theory and experiment at a few of the frequencies actually used. The same authors have also suggested[16] that the Kleinman symmetry conjecture for macroscopic susceptibilities (i.e., their invariance to the interchange of the spatial indexes)[17] may also apply to the molecular-axial indexes on the microscopic hyperpolarizabilities. This we can check directly and simply by calculating all the hyperpolarizability components. Furthermore, since we have results for several processes at several frequencies, we will explore the sufficiency of the approximation:[18]

$$\bar{\chi}^{(3)}_{\parallel}=A+B\omega_L^2+C\omega_L^4+\cdots\ , \qquad (2)$$

where

$$\omega_L^2=\omega_\sigma^2+\omega_1^2+\omega_2^2+\omega_3^2\ .$$

A final objective for the work reported is to lay to rest any doubts concerning the fundamental theory which may have been suscitated by the widely differing theoretical and experimental results for FH.[19,20]

In Sec. II we give the basic formulas we have used—these rest on the Orr-Ward[3] perturbation formulation of the hyperpolarizabilities. We describe our wave functions, which are the James-Coolidge type (i.e., they explicitly include the interelectronic coordinate) and hence directly incorporate electron correlation.

In Sec. III we give the dynamic dipole polarizability components and the hyperpolarizability components (for the four processes: dc Kerr, DFWM, ESHG, THG) for six internuclear distances and four frequencies for $H_2$. These hyperpolarizability components are then combined to obtain values for $H_2$ and $D_2$ which can be compared with experiment. In the same section we discuss various aspects of our results, as well as making comparisons with previous work. We also report calculated "vibrational" contributions.

Our final results assume a rotational state population appropriate to $T=22\,^\circ\mathrm{C}$ and we have assumed that only the ground vibrational state is populated. We believe, taking into consideration the convergence of what is a very flexible basis set, that our values have an accuracy of 1% or better—and this exceeds, in most cases, the accuracy of the experiments. In Sec. IV we draw some conclusions. In general we use atomic units: $a_0=1$ bohr $\simeq 0.529\,177$ Å, dipole polarizability $\alpha=e^2a_0^2E_h^{-1}$ $\simeq 1.6488\times10^{-41}$ $\mathrm{C^2m^2J^{-1}}$, hyperpolarizability $\gamma=e^4a_0^4E_h^{-3}$ $\simeq 5.0372\times10^{-40}$ esu $\simeq 0.623\,60\times10^{-64}$ $\mathrm{C^4m^4J^{-3}}$.

## II. THEORY AND METHOD

In this section we introduce our notation and working formulas; the first step is to relate the macroscopic susceptibilities $\bar{\chi}_{\parallel}^{(3)}$ of Eq. (1) to the microscopic hyperpolarizabilities $\gamma_{\alpha\beta\gamma\delta}$, where the indexes $\alpha,\beta,\gamma,\delta$ denote the molecular axes $x$, $y$, and $z$ with the latter lying along the nuclear axis. Since we are dealing with $H_2$ and $D_2$, our relations will be those pertinent for a molecule with $D_{\infty h}$ symmetry and will contain no $kT$ second-order component.

$\bar{\chi}_{\parallel}^{(3)}$ will be a temperature-dependent quantity: a Maxwell-Boltzmann average over the populated rotational levels as labeled by the quantum number $J$, that is,

$$\bar{\chi}_{\parallel}^{(3)}=\sum_{J=0}\rho(J)\chi_{\parallel}^{(3)}(J)\ , \tag{3}$$

where

$$\rho(J)=\frac{g_J(2J+1)\exp(-\Delta E_J/kT)}{\sum_J g_J(2J+1)\exp(-\Delta E_J/kT)} \tag{4}$$

and $g_J$ is the nuclear spin factor; it equals 3 for odd $J$ and for even $J$ it equals 1 for $H_2$ and 6 for $D_2$. $\Delta E_J$ are the rotational energy level spacings. $\chi_{\parallel}^{(3)}(J)$ is then the expectation value of the isotropic hyperpolarizability $\bar{\gamma}_{\parallel}(R)$, a function of the internuclear separation $R$, over the vibrational-rotational wave function $|v,J\rangle$. We will assume that only the lowest vibrational state ($v=0$) is of interest, so that

$$\chi_{\parallel}^{(3)}(J)=\langle 0,J\,|\,\bar{\gamma}_{\parallel}(R)\,|\,0,J\rangle\ . \tag{5}$$

The isotropic hyperpolarizability $\bar{\gamma}_{\parallel}(R)$ is

$$\bar{\gamma}_{\parallel}(R)=\bar{\gamma}=(\gamma_{\xi\xi\eta\eta}+\gamma_{\xi\eta\xi\eta}+\gamma_{\xi\eta\eta\xi})/15\ , \tag{6}$$

where, for simplicity, we have dropped the "parallel" subscript and the Greek (molecular-axial) subscripts can be equal to $x,y,z$ with a repeated subscript indicating a summation over all three Cartesian components. It should be noted that there is more than one convention for the definition of the susceptibilities and hyperpolarizabilities and that the one we have adopted here leads to hyperpolarizability values in keeping with Buckingham's definition[21] but six times larger than those of Ward and co-workers.[3,7] The diatomic symmetry and the allowable permutations of the indexes for the property at hand leads to

$$\bar{\gamma}(-\omega;0,0,\omega)=(8\gamma_{xxxx}+8\gamma_{xxzz}+2\gamma_{xzzx}+2\gamma_{zxxz}+3\gamma_{zzzz})/15\ , \tag{7a}$$

since

$$\gamma_{xxzz}=\gamma_{zzxx}=\gamma_{xzxz}=\gamma_{zxzx}\ ; \tag{7b}$$

$$\bar{\gamma}(-\omega;\omega,\omega,-\omega)=(8\gamma_{xxxx}+8\gamma_{xxzz}+4\gamma_{xzzx}+3\gamma_{zzzz})/15\ , \tag{8a}$$

since

$$\gamma_{xxzz}=\gamma_{zzxx}=\gamma_{xzxz}=\gamma_{zxzx}\ , \tag{8b}$$

$$\gamma_{xzzx}=\gamma_{zxxz}\ ; \tag{8c}$$

$$\bar{\gamma}(-2\omega;0,\omega,\omega)=(8\gamma_{xxxx}+2\gamma_{xxzz}+2\gamma_{zzxx}+4\gamma_{xzzx}+4\gamma_{zxxz}+3\gamma_{zzzz})/15\ , \tag{9a}$$

since

$$\gamma_{xzzx}=\gamma_{xzxz}\ , \tag{9b}$$

$$\gamma_{zxxz}=\gamma_{zxzx}\ ; \tag{9c}$$

$$\bar{\gamma}(-3\omega;\omega,\omega,\omega)=(8\gamma_{xxxx}+6\gamma_{xxzz}+6\gamma_{zzxx}+3\gamma_{zzzz})/15\ , \tag{10a}$$

since

$$\gamma_{xxzz}=\gamma_{xzxz}=\gamma_{xzzx}\ , \tag{10b}$$

$$\gamma_{zzxx}=\gamma_{zxzx}=\gamma_{zxxz}\ . \tag{10c}$$

We will calculate all the necessary independent components $\gamma_{\alpha\beta\gamma\delta}$ for each process by means of Orr and Ward's[3,16] formula:

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\hbar^{-3}\sum_P\left[\sum_{m,n,p,(\neq g)}\frac{\langle g|\mu_\alpha|m\rangle\langle m|\bar{\mu}_\delta|n\rangle\langle n|\bar{\mu}_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1-\omega_2)(\omega_{pg}-\omega_1)}-\sum_{m,n(\neq g)}\frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1)(\omega_{ng}+\omega_2)}\right]\ , \tag{11}$$

TABLE I. Convergence of the third-order static hyperpolarizabilities of $H_2$ (in atomic units) for $R=1.4a_0$.

| Number of basis functions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\Sigma_g^+$ | $\Sigma_u^+$ | $\Pi_u$ | $\Pi_g$ | $\Delta_g$ | $\gamma_{xxxx}$ | $\gamma_{xxzz}$ | $\gamma_{zzzz}$ | $\bar{\gamma}$ |
| 54 | 34 | 34 | 34 | 34 | 525.0 | 143.1 | 520.0 | 498.5 |
| 54 | 64 | 64 | 64 | 64 | 528.0 | 189.6 | 520.4 | 537.4 |
| 54 | 94 | 94 | 94 | 94 | 528.4 | 207.2 | 520.9 | 551.8 |
| 54 | 113 | 124 | 124 | 124 | 528.8 | 212.8 | 521.1 | 556.5 |
| 54 | 113 | 124 | 154 | 124 | 528.8 | 215.7 | 521.1 | 558.8 |
| 54 | 113 | 124 | 160 | 124 | 528.8 | 215.9 | 521.1 | 559.0 |
| 84 | 113 | 124 | 160 | 124 | 563.0 | 200.8 | 676.3 | 596.2 |
| 114 | 113 | 124 | 160 | 124 | 563.4 | 200.7 | 678.1 | 596.7 |
| 144 | 113 | 124 | 160 | 124 | 563.4 | 200.6 | 678.5 | 596.7 |
| 174 | 113 | 124 | 160 | 124 | 564.2 | 200.1 | 682.0 | 597.4 |
| 204 | 113 | 124 | 160 | 124 | 564.3 | 200.0 | 682.3 | 597.4 |
| 249 | 113 | 124 | 160 | 124 | 564.3 | 200.0 | 682.5 | 597.5 |

where $\sum_P$ implies a summation over the 24 terms generated by permuting the frequencies with their associated spatial subscripts, $\mu_\alpha$ is the $\alpha$ component of the electric dipole moment operator, $|m\rangle$ is an electronic wave function, and

$$\langle m|\bar{\mu}_\delta|n\rangle=\langle m|\mu_\delta|n\rangle-\delta_{mn}\langle g|\mu_\delta|g\rangle \ .$$

In our case ( a nondipolar molecule) the bars in Eq. (11) can be dropped.

Since we will briefly mention in Sec. III the dynamic dipole polarizabilities, the equivalent formula for them is

$$\alpha_{\alpha\beta}(-\omega;\omega)=\hbar^{-1}\sum_P \sum_{m(\neq g)} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle}{(\omega_{mg}-\omega)} \ . \qquad (12)$$

The remaining, but key problem, is therefore to determine sufficiently accurate ground and excited (of appropriate symmetry) electronic wave functions for use in Eqs. (11) and (12). The choice is critical since hyperpolarizabilities are extremely sensitive properties— this was clearly demonstrated some years ago by one of us in a calculation of the static $\gamma_{zzzz}$ component for $H_2$.[22] We will use James-Coolidge-type wave functions which are composed of basis functions which explicitly include the interelectronic coordinate $r_{12}$ and thus directly incorporate electron correlation. Such wave functions have shown their superiority and accuracy for small systems in numerous calculations.[23–25]

We will find them by solving the Schrödinger equation variationally for states of the following symmetries: $\Sigma_g^+$ (ground state), $\Sigma_u^+$ (for the intermediate states needed for $\gamma_{zzzz}$), $\Pi_u$ and $\Delta_g$ (for the intermediate states in $\gamma_{xxxx}$), and $\Sigma_u^+$, $\Pi_u$ (again), and $\Pi_g$ (for the intermediate states in the mixed components). The $\Pi_u$ and $\Sigma_u^+$ states will also

TABLE II. Dynamic dipole polarizability of $H_2$ as a function of the internuclear distance $R$, in atomic units.

| λ (Å) | $\alpha_{xx}$ | $\alpha_{zz}$ | $\alpha_{xx}$ | $\alpha_{zz}$ |
|---|---|---|---|---|
| | $R=0.40$ | | $R=1.40$ | |
| ∞ | 1.857 740 | 1.939 037 | 4.578 492[a] | 6.387 493[b] |
| 6943 | 1.869 270 | 1.951 294 | 4.642 811 | 6.494 329 |
| 6328 | 1.871 640 | 1.953 815 | 4.656 173[c] | 6.516 581[d] |
| 4880 | 1.881 251 | 1.964 037 | 4.710 855 | 6.607 843 |
| | $R=1.0$ | | $R=1.45$ | |
| ∞ | 3.341 975[e] | 4.092 918[f] | 4.740 029 | 6.722 980 |
| 6943 | 3.377 129 | 4.140 124 | 4.808 782 | 6.840 480 |
| 6328 | 3.384 398 | 4.149 895 | 4.823 074 | 6.864 975 |
| 4880 | 3.414 022 | 4.189 751 | 4.881 593 | 6.965 513 |
| | $R=1.35$ | | $R=2.40$ | |
| ∞ | 4.417 948 | 6.062 466 | 7.659 246[g] | 14.269 08[h] |
| 6943 | 4.477 998 | 6.159 447 | 7.833 021 | 14.775 08 |
| 6328 | 4.490 466 | 6.179 629 | 7.869 528 | 14.882 76 |
| 4880 | 4.541 460 | 6.262 340 | 8.020 404 | 15.332 99 |

[a]Best previous result: 4.578 557 (Ref. 27).
[b]Best previous result: 6.387 319 (Ref. 30).
[c]Best previous result: 4.656 221 (Ref. 30).
[d]Best previous result: 6.516 384 (Ref. 30).
[e]Best previous result: 3.342 282 1 (Ref. 29).
[f]Best previous result: 4.092 760 0 (Ref. 29).
[g]Best previous result: 7.660 486 8 (Ref. 29).
[h]Best previous result: 14.266 208 8 (Ref. 29).

be required for calculating $\alpha_{xx}$ and $\alpha_{zz}$, respectively. The number of states we take for each symmetry, and then use in Eqs. (11) and (12), is equal to the size of the basis set used in solving the Schrödinger equation.

The basis functions are defined by the following equations:

$$\psi_i^\sigma(1,2)=\exp[-\alpha(\xi_1+\xi_2)]\xi_1^{m_i}\xi_2^{n_i}\eta_1^{k_i}\eta_2^{l_i}\rho^{q_i} \ , \tag{13a}$$

$$\psi_i^\pi(1,2)=\psi_i^\sigma(1,2)[(\xi_1^2-1)(1-\eta_1^2)]^{1/2}\cos\phi_1 \ , \tag{13b}$$

$$\psi_i^\delta(1,2)=\psi_i^\sigma(1,2)[(\xi_1^2-1)(1-\eta_1^2)]\cos(2\phi_1) \ , \tag{13c}$$

where $\xi_1,\eta_1,\phi_1$ are elliptical coordinates for electron 1, $\rho=2r_{12}/R$ ($r_{12}$ is the interelectronic coordinate and $R$ is the internuclear distance), $m$, $n$, $k$, $l$, and $q$ are integers which define the basis functions, and $\alpha$ is a nonlinear parameter to be optimized. The wave functions are written as the following linear combinations:

$$\Psi(\Sigma_g^+)=\sum_{i=1}^{249}a_i[(1+P_{12})\psi_i^\sigma(1,2)] \ , \quad k_i+l_i \text{ even} \tag{14a}$$

$$\Psi(\Sigma_u^+)=\sum_{i=1}^{113}b_i[(1+P_{12})\psi_i^\sigma(1,2)] \ , \quad k_i+l_i \text{ odd} \tag{14b}$$

$$\Psi(\Pi_u)=\sum_{i=1}^{124}c_i[(1+P_{12})\psi_i^\pi(1,2)] \ , \quad k_i+l_i \text{ even} \tag{14c}$$

$$\Psi(\Pi_g)=\sum_{i=1}^{160}d_i[(1+P_{12})\psi_i^\pi(1,2)] \ , \quad k_i+l_i \text{ odd} \tag{14d}$$

$$\Psi(\Delta_g)=\sum_{i=1}^{124}e_i[(1+P_{12})\psi_i^\delta(1,2)] \ , \quad k_i+l_i \text{ even} \ , \tag{14e}$$

where $P_{12}$ is the electron permutation operator. The number of terms shown in these sums is that used in the final calculations and will be discussed shortly.

For the nonlinear parameter $\alpha$, the value for $R=1.35a_0$, $1.40a_0$, $1.45a_0$ was taken to be 1.027. This value had been previously determined by Kołos and Wolniewicz in a ground-state energy calculation[24] and subsequently and successfully used by them in a static dipole polarizability calculation.[26] At other internuclear dis-

TABLE III. Hyperpolarizabilities $\gamma(-\omega;0,0,\omega)$ for $H_2$ as functions of the internuclear distance $R$, in atomic units.

| λ (Å) | $\gamma_{xxxx}$ | $\gamma_{xxzz}$ | $\gamma_{xzzx}$ | $\gamma_{zxxz}$ | $\gamma_{zzzz}$ | $\bar{\gamma}$ |
|---|---|---|---|---|---|---|
| | | | $R$ =0.40 | | | |
| ∞ | 76.5 | 22.0 | 22.0 | 22.0 | 80.1 | 74.4 |
| 6943 | 78.3 | 22.6 | 22.3 | 22.4 | 82.0 | 76.2 |
| 6328 | 78.6 | 22.7 | 22.4 | 22.4 | 82.4 | 76.5 |
| 4880 | 80.1 | 23.1 | 22.7 | 22.7 | 84.0 | 77.9 |
| | | | $R$ =1.00 | | | |
| ∞ | 278 | 90.3 | 90.3 | 90.3 | 314 | 283 |
| 6943 | 289 | 94.1 | 92.8 | 93.1 | 327 | 295 |
| 6328 | 291 | 94.9 | 93.4 | 93.8 | 330 | 297 |
| 4880 | 300 | 98.2 | 95.6 | 96.3 | 342 | 306 |
| | | | $R$ =1.35 | | | |
| ∞ | 521 | 182 | 182 | 182 | 624 | 548 |
| 6943 | 547 | 192 | 189 | 190 | 658 | 576 |
| 6328 | 553 | 194 | 190 | 192 | 666 | 583 |
| 4880 | 576 | 203 | 197 | 199 | 669 | 607 |
| | | | $R$ =1.40 | | | |
| ∞ | 564 | 200 | 200 | 200 | 683 | 597 |
| 6943 | 594 | 211 | 208 | 210 | 722 | 629 |
| 6328 | 600 | 214 | 210 | 212 | 730 | 636 |
| 4880 | 627 | 224 | 217 | 220 | 766 | 665 |
| | | | $R$ =1.45 | | | |
| ∞ | 610 | 219 | 219 | 219 | 745 | 650 |
| 6943 | 643 | 232 | 228 | 230 | 790 | 686 |
| 6328 | 650 | 235 | 230 | 233 | 799 | 694 |
| 4880 | 680 | 246 | 239 | 243 | 839 | 726 |
| | | | $R$ =2.40 | | | |
| ∞ | 1793 | 754 | 754 | 754 | 3137 | 2187 |
| 6943 | 1942 | 826 | 801 | 823 | 3447 | 2382 |
| 6328 | 1974 | 842 | 812 | 838 | 3516 | 2425 |
| 4880 | 2113 | 911 | 855 | 903 | 3812 | 2610 |

tances $\alpha$ was chosen by minimizing the ground-state energy with a 107-term basis set described, with the notation of Bishop and Cheung,[25] as (6342/5). This led to the values $\alpha=0.411$, 0.879, and 1.622 at $R=0.4a_0$, $1.0a_0$, and $2.4a_0$, respectively.

The choice of basis functions selected for the final wave functions in Eq. (14) was based on the convergence of the static hyperpolarizabilities at $R=1.4a_0$. Initially, we started with the 54-term selection of Kołos and Wolniewicz[24] for $\Psi(\Sigma_g^+)$ and their 34-term selection[26] for the other states. Our final selection consisted of addition to these sets of all nonrepetitive terms appearing in the sets (6453/7) for $\Sigma_g^+$, (6453/5) for $\Sigma_u^+$, (5342/5) for $\Pi_u$, (6453/6) for $\Pi_g$, and (5342/5) for $\Delta_g$, i.e., 249, 113, 124, 160, and 124 terms, respectively. Convergence, using intermediate-sized basis sets (adding 30 terms at a time) is shown in Table I and justifies our final choice.

So far, we have not explicitly discussed the distortion of the nuclear frame by the electric fields. If in Eq. (11) we replace the electronic wave functions by the complete rovibronic wave functions, which would be the rigorous thing to do, then the summation can be split into three parts which can be crudely identified as electronic, rotational, and vibrational.[27] The first part, where the intermediate states involve *excited* electronic states, is what we have so far been considering. The second part, which involves intermediate states with ground electronic and vibrational wave functions, is commonly called orientational polarization[4]—a temperature-dependent contribution which is separated from the experimental data. The third part (once unfortunately termed atomic polarizability) comes from intermediate states having the *ground* electronic wave function but *excited* vibrational wave functions. It is a result of nuclear displacement by the applied fields and is in addition to the averaging accomplished in Eq. (5). Approximate formulas (equivalent to assuming a classical orientational average) for this contribution have been established by Bishop[8,9] and Shelton[28] for the third-order susceptibilities. They are

$$\chi^{v}_{\parallel}(-\omega,0,0,\omega)=\sum_{k}2a_k[(\omega_k-\omega)^{-1}+(\omega_k+\omega)^{-1}+\omega_k^{-1}]/15\hbar\ , \tag{15a}$$

TABLE IV. Hyperpolarizabilities $\gamma(-\omega;\omega,\omega,-\omega)$ for $H_2$ as functions of the internuclear distance $R$, in atomic units.

| λ (Å) | $\gamma_{xxxx}$ | $\gamma_{xxzz}$ | $\gamma_{xzzx}$ | $\gamma_{zzzz}$ | $\bar{\gamma}$ |
|---|---|---|---|---|---|
| | | | $R=0.40$ | | |
| ∞ | 76.5 | 22.0 | 22.0 | 80.1 | 74.4 |
| 6943 | 80.1 | 22.7 | 23.6 | 84.0 | 77.9 |
| 6328 | 80.9 | 22.8 | 23.9 | 84.8 | 78.6 |
| 4880 | 84.1 | 23.4 | 25.3 | 88.2 | 81.7 |
| | | | $R=1.00$ | | |
| ∞ | 278 | 90.3 | 90.3 | 314 | 283 |
| 6943 | 300 | 95.8 | 100 | 341 | 306 |
| 6328 | 305 | 97.0 | 103 | 347 | 311 |
| 4880 | 326 | 102 | 113 | 372 | 333 |
| | | | $R=1.35$ | | |
| ∞ | 521 | 182 | 182 | 624 | 548 |
| 6943 | 576 | 198 | 208 | 696 | 607 |
| 6328 | 588 | 201 | 214 | 712 | 620 |
| 4880 | 641 | 216 | 240 | 782 | 677 |
| | | | $R=1.40$ | | |
| ∞ | 564 | 200 | 200 | 683 | 507 |
| 6943 | 626 | 218 | 229 | 765 | 664 |
| 6328 | 640 | 222 | 236 | 783 | 679 |
| 4880 | 700 | 239 | 266 | 864 | 745 |
| | | | $R=1.45$ | | |
| ∞ | 610 | 219 | 219 | 745 | 650 |
| 6943 | 679 | 240 | 252 | 838 | 725 |
| 6328 | 695 | 245 | 260 | 859 | 742 |
| 4880 | 763 | 265 | 294 | 952 | 817 |
| | | | $R=2.40$ | | |
| ∞ | 1793 | 754 | 754 | 3137 | 2187 |
| 6943 | 2110 | 875 | 943 | 3798 | 2603 |
| 6328 | 2185 | 903 | 990 | 3956 | 2702 |
| 4880 | 2530 | 1028 | 1213 | 4691 | 3159 |

$$\chi_{\parallel}^{v}(-\omega;\omega,\omega,-\omega)=\sum_{k}a_{k}[(\omega_{k}-2\omega)^{-1}+(\omega_{k}+2\omega)^{-1}+4\omega_{k}^{-1}]/15\hbar\ , \qquad (15b)$$

$$\chi_{\parallel}^{v}(-2\omega;0,\omega,\omega)=\sum_{k}a_{k}[2(\omega_{k}-\omega)^{-1}+2(\omega_{k}+\omega)^{-1}+(\omega_{k}-2\omega)^{-1}+(\omega_{k}+2\omega)^{-1}]/15\hbar\ , \qquad (15c)$$

$$\chi_{\parallel}^{v}(-3\omega;\omega,\omega,\omega)=\sum_{k}3a_{k}[(\omega_{k}-2\omega)^{-1}+(\omega_{k}+2\omega)^{-1}]/15\hbar\ , \qquad (15d)$$

where

$$a_{k}=8\langle\alpha_{xx}\rangle_{0k}^{2}+4\langle\alpha_{xx}\rangle_{0k}\langle\alpha_{zz}\rangle_{0k}+3\langle\alpha_{zz}\rangle_{0k}^{2}\ . \qquad (16)$$

The summations run over the vibrational excited states ($k$) with frequencies $\omega_k$ and $\langle\alpha_{xx}\rangle_{0k}$ is the vibrational static dipole polarizability transition element, i.e., $\langle 0,0|\alpha_{xx}|k,0\rangle$. That the exclusion of excited rotational states ($J\neq 0$) from these equations is a good approximation for $H_2$ and $D_2$ has been demonstrated by Shelton,[28] who also considered a freely rotating molecule; unlike his evaluations, however, we do sum over more than just the first vibrational excited state. We will therefore use Eq. (15) for evaluating the vibrational susceptibilities.

## III. RESULTS AND DISCUSSION

In Table II we give our dynamic dipole polarizability ($\alpha$) results for $R=0.4a_0$, $1.0a_0$, $1.35a_0$, $1.40a_0$, $1.45a_0$ and $2.4a_0$ and $\lambda=\infty$, 6943, 6328, and 4880 Å. Though not directly germane to this work, they are a useful indication of the accuracy of our wave functions. They were obtained from Eq. (12) with a 249-term $\Sigma_g^+$ ground-state wave function, and 113 $\Sigma_u^+$ and 124 $\Pi_u$ intermediate states. Where comparison with the previous accurate results of Rychlewski[29,30] and Bishop and Cheung[27] can be

TABLE V. Hyperpolarizabilities $\gamma(-2\omega;0,\omega,\omega)$ for $H_2$ as functions of the internuclear distance $R$, in atomic units.

| λ (Å) | $\gamma_{xxxx}$ | $\gamma_{xxzz}$ | $\gamma_{xzzx}$ | $\gamma_{zxxz}$ | $\gamma_{zzxx}$ | $\gamma_{zzzz}$ | $\bar{\gamma}$ |
|---|---|---|---|---|---|---|---|
| | | | | $R=0.40$ | | | |
| ∞ | 76.5 | 22.0 | 22.0 | 22.0 | 22.0 | 80.1 | 74.4 |
| 6943 | 82.0 | 23.9 | 23.3 | 23.3 | 24.0 | 86.0 | 79.7 |
| 6328 | 83.2 | 24.4 | 23.5 | 23.6 | 24.4 | 87.3 | 80.9 |
| 4880 | 88.2 | 26.2 | 24.7 | 24.8 | 26.2 | 92.7 | 85.8 |
| | | | | $R=1.00$ | | | |
| ∞ | 278 | 90.3 | 90.3 | 90.3 | 90.3 | 314 | 283 |
| 6943 | 312 | 103 | 99.6 | 100 | 104 | 356 | 318 |
| 6328 | 320 | 106 | 102 | 103 | 107 | 365 | 327 |
| 4880 | 354 | 120 | 111 | 112 | 121 | 406 | 362 |
| | | | | $R=1.35$ | | | |
| ∞ | 521 | 182 | 182 | 182 | 182 | 624 | 548 |
| 6943 | 606 | 216 | 208 | 211 | 218 | 736 | 640 |
| 6328 | 626 | 225 | 213 | 217 | 227 | 762 | 661 |
| 4880 | 715 | 262 | 240 | 247 | 266 | 883 | 758 |
| | | | | $R=1.40$ | | | |
| ∞ | 564 | 200 | 200 | 200 | 200 | 683 | 597 |
| 6943 | 660 | 239 | 230 | 233 | 241 | 811 | 702 |
| 6328 | 683 | 249 | 236 | 241 | 251 | 841 | 726 |
| 4880 | 785 | 292 | 267 | 276 | 297 | 980 | 838 |
| | | | | $R=1.45$ | | | |
| ∞ | 610 | 219 | 219 | 219 | 219 | 745 | 650 |
| 6943 | 718 | 263 | 253 | 257 | 266 | 891 | 768 |
| 6328 | 743 | 274 | 261 | 266 | 277 | 926 | 795 |
| 4880 | 858 | 323 | 296 | 307 | 330 | 1086 | 923 |
| | | | | $R=2.40$ | | | |
| ∞ | 1793 | 754 | 754 | 754 | 754 | 3137 | 2187 |
| 6943 | 2297 | 1008 | 940 | 995 | 1039 | 4213 | 2857 |
| 6328 | 2424 | 1074 | 985 | 1057 | 1116 | 4496 | 3029 |
| 4880 | 3048 | 1410 | 1204 | 1375 | 1521 | 5963 | 3897 |

TABLE VI. Hyperpolarizabilities $\gamma(-3\omega;\omega,\omega,\omega)$ for $H_2$ as functions of the internuclear distance $R$, in atomic units.

| λ (Å) | $\gamma_{xxxx}$ | $\gamma_{xxzz}$ | $\gamma_{zzxx}$ | $\gamma_{zzzz}$ | $\bar{\gamma}$ |
|---|---|---|---|---|---|
| | | | $R=0.40$ | | |
| ∞ | 76.5 | 22.0 | 22.0 | 80.1 | 74.4 |
| 6943 | 88.0 | 25.1 | 25.2 | 92.5 | 85.6 |
| 6328 | 90.7 | 25.9 | 25.9 | 95.3 | 88.2 |
| 4880 | 103 | 29.1 | 29.3 | 108 | 99.9 |
| | | | $R=1.00$ | | |
| ∞ | 278 | 90.3 | 90.3 | 314 | 283 |
| 6943 | 353 | 113 | 115 | 405 | 360 |
| 6328 | 371 | 119 | 121 | 428 | 379 |
| 4880 | 462 | 147 | 152 | 541 | 474 |
| | | | $R=1.35$ | | |
| ∞ | 521 | 182 | 182 | 624 | 548 |
| 6943 | 712 | 245 | 253 | 879 | 755 |
| 6328 | 762 | 262 | 272 | 948 | 810 |
| 4880 | 1027 | 349 | 376 | 1324 | 1103 |
| | | | $R=1.40$ | | |
| ∞ | 564 | 200 | 200 | 683 | 597 |
| 6943 | 780 | 273 | 282 | 976 | 833 |
| 6328 | 838 | 292 | 305 | 1056 | 897 |
| 4880 | 1145 | 395 | 428 | 1501 | 1240 |
| | | | $R=1.45$ | | |
| ∞ | 610 | 219 | 219 | 745 | 650 |
| 6943 | 853 | 303 | 314 | 1080 | 918 |
| 6328 | 919 | 325 | 340 | 1174 | 991 |
| 4880 | 1272 | 445 | 486 | 1698 | 1390 |
| | | | $R=2.40$ | | |
| ∞ | 1793 | 754 | 754 | 3137 | 2187 |
| 6943 | 3020 | 1250 | 1435 | 5949 | 3874 |
| 6328 | 3409 | 1406 | 1682 | 6972 | 4448 |
| 4880 | 5992 | 2438 | 3824 | 15830 | 8867 |

made, it appears that our $\alpha_{zz}$ component is always superior (a larger value) and there is also very good agreement (five significant figures at $R=1.4a_0$) for the $\alpha_{xx}$ component.

In Tables III–VI we give our major results, which in nearly all cases are new ones. They are the electronic hyperpolarizability tensors for $H_2$, defined by Eq. (11), and the isotropic values $\bar{\gamma}$, defined by Eqs. (7)–(10), for $R=0.4a_0$, $1.0a_0$, $1.35a_0$, $1.40a_0$, $1.45a_0$, and $2.4a_0$ and $\lambda=\infty$, 6943, 6328, and 4880 Å. They are based on the electronic wave functions of Eq. (14) and concern the nonlinear optical experiments: dc Kerr (Table III), DFWM (Table IV), ESHG (Table V), and THG (Table VI).

TABLE VII. Thermally averaged values of powers of the internuclear distance, $\overline{R^n}$, at $T=22\,^{\circ}\mathrm{C}$.

| | $H_2$ | $D_2$ |
|---|---|---|
| $\overline{R}$ | 1.4522 | 1.4381 |
| $\overline{R^2}$ | 2.1371 | 2.0880 |
| $\overline{R^3}$ | 3.1866 | 3.0600 |

To evaluate the averages of $\bar{\gamma}(R)$ over the rotational-vibrational wave functions $|0,J\rangle$, as in Eq. (7), we have fitted the six $\bar{\gamma}(R)$ for each of the four phenomena to the equation:

$$\bar{\gamma}(R)=a+bR+cR^2+dR^3\ , \tag{17}$$

(the values of $a,b,c,d$ are given in the Appendix) and then, using known values[31,32] of the integrals $\langle 0,J\,|\,R^n\,|\,0,J\rangle$ and the rotational energies $E_J^{31}$, we have found

$$\overline{R^n}=\sum_J \rho(J)\langle 0,J\,|\,R^n\,|\,0,J\rangle,\ n=1,2,3 \tag{18}$$

where $\rho(J)$ is defined in Eq. (4). Values for $H_2$ and $D_2$ are given in Table VII for $T=22\,^{\circ}\mathrm{C}$, which is the temperature of the ESHG experiment.[15] $\bar{\chi}_{\parallel}^{(3)}$ is then found from

$$\bar{\chi}_{\parallel}^{(3)}=a+b\overline{R}+c\overline{R^2}+d\overline{R^3}\ . \tag{19}$$

Values for $H_2$ and $D_2$ are displayed in Table VIII for the

TABLE VIII. Values of $\bar{\chi}_{\parallel}^{(3)}$ for various nonlinear processes at $T=22\,^{\circ}\mathrm{C}$ in atomic units. (The purely vibrational component is not included.)

| | $\bar{\chi}_{\parallel}^{(3)}(-\omega;0,0,\omega)$ | | $\bar{\chi}_{\parallel}^{(3)}(-\omega;\omega,\omega,-\omega)$ | | $\bar{\chi}_{\parallel}^{(3)}(-2\omega;0,\omega,\omega)$ | | $\bar{\chi}_{\parallel}^{(3)}(-3\omega;\omega,\omega,\omega)$ | |
|---|---|---|---|---|---|---|---|---|
| λ (Å) | $H_2$ | $D_2$ | $H_2$ | $D_2$ | $H_2$ | $D_2$ | $H_2$ | $D_2$ |
| ∞ | 666 | 647 | 666 | 647 | 666 | 647 | 666 | 647 |
| 6943 | 704 | 683 | 746 | 723 | 792 | 766 | 954 | 920 |
| 6328 | 713 | 691 | 764 | 740 | 821 | 794 | 1035 | 995 |
| 4880 | 747 | 724 | 844 | 816 | 959 | 924 | (1502)[a] | (1425)[a] |

[a] May be less accurate than the other results, since $3\omega$ is approaching the lowest electronic excitation energy at $R>2.0a_0$.

four processes at λ = ∞, 6943, 6328, and 4880 Å—they should be directly comparable with experiment in those cases where the pure vibrational contributions, Eq. (15), are small or have been extracted from the experimental data (we will discuss this point later). We believe that our accuracy, on the basis of the convergency tests, is 1% or better.

In comparing our results with the few calculations which exist in the literature, we will start with the static values (λ = ∞). Using the same basis functions as here, Bishop and Cheung[22] obtained $\gamma_{zzzz}=674$ a.u. at $R=1.4a_0$; since that work shows that convergence for *this* component is from below, our present value of 683 a.u. is considered to be better. Berns and Wormer[33] have made a very thorough study of the static hyperpolarizabilities of $H_2$ using the finite-field method and a full configurational-interaction (CI) wave function with a ($10s4p2d$) Gaussian basis set. The same basis, without scaling, was used at all internuclear distances. As is seen in Table IX, their results are very similar to ours. They can be used to obtain $\bar{\chi}_{\parallel}^{(3)}(0)$, leading to the values 672($H_2$) and 652($D_2$), where we have 666($H_2$) and 647($D_2$) at $T=22\,^{\circ}\mathrm{C}$. Watts and Stelbovics,[10] in a random-phase-approximation treatment (which many consider accounts for only first-order electron correlation effects) and using a 42-term basis set, obtained for $R=1.4a_0$ results distinctly different from ours (and those of Berns and Wormer), i.e., 610, 183, and 330 a.u. for $\gamma_{xxxx}$, $\gamma_{xxzz}$, and $\gamma_{zzzz}$, respectively. They also computed (assuming Kleinman microsymmetry) the ESHG susceptibility at λ = 6943 Å. But in the light of their static values, their result of $\bar{\gamma}_{\parallel}(R=1.4a_0)=702$ must be reckoned as *fortuitously* good (cf. Table V).

TABLE IX. Comparison of the static hyperpolarizability $\gamma$ of $H_2$ with previous work (atomic units).

| | $R$ | This work | Ref. 33 | Ref. 11 |
|---|---|---|---|---|
| $\gamma_{xxxx}$ | 1.4 | 564 | 557 | 572 |
| $\gamma_{xxzz}$ | 1.4 | 200 | 211 | 225 |
| $\gamma_{zzzz}$ | 1.4 | 683[a] | 686 | 689[b] |
| $\bar{\gamma}$[c] | 1.4 | 597 | 603[d] | 623 |
| | 1.0 | 283 | 292 | 304 |
| | 2.4 | 2187 | 2183 | 2265 |

[a] Previously, the best static value of this component (using similar wave functions as here) was 674 (Ref. 22).

[b] The value 666.8 given in Table 7 of Ref. 11 should be 688.8 as in their Table 6.

[c] $\bar{\gamma}=(8\gamma_{xxxx}+12\gamma_{xxzz}+3\gamma_{zzzz})/15$.

[d] $\bar{\gamma}$ is found from Ref. 33 by using $9G_0/5$.

Jaszuński and Roos[11] made both static and dynamic calculations for DFWM and THG for $H_2$ (in fact, the only previous theoretical study of these properties). They used a steady-state formulation of the time-dependent Schrödinger equation, which is equivalent to the approach taken here, provided the summations are over the entire CI space. With full CI wave functions and basis sets of the type ($12s6p3d$), they obtained results said to be accurate to a few percent. Calculations were made for $R=1.0a_0$, $1.2a_0$, $1.4a_0$, $1.6a_0$, $2.0a_0$ and $2.4a_0$ (using the same basis for each distance) and a range of frequencies. Some of their static values are compared with ours in Table IX and are always larger than both ours and those of Berns and Wormer, e.g., their $\bar{\gamma}$ is 4% greater at $R=1.4a_0$. In Table X we compare their dynamic values of $\gamma(-\omega;\omega,\omega,-\omega)$, $\gamma(-3\omega;\omega,\omega,\omega)$, and $\bar{\gamma}(-3\omega;\omega,\omega,\omega)$ with our results. We cannot compare $\bar{\gamma}(-\omega;\omega,\omega,-\omega)$ since they did not report the $\gamma_{xzzx}$ component which is needed for this quantity. Their results are again consistently higher than ours, e.g., $\bar{\gamma}(-3\omega;\omega,\omega,\omega)$ is 5% greater at λ = 6943 Å. The largest differences occur for the mixed components. Their values lead to $\bar{\chi}_{\parallel}^{(3)}(0)=693$ for $H_2$, where we have 666 a.u.

Of much more interest, perhaps, is to make comparison with the available experimental data. Ward and New[34] in THG experiments found $\bar{\chi}_{\parallel}^{(3)}(-3\omega;\omega,\omega,\omega)$ at 6943 Å to be 950±140 (we have multiplied their value by 6 to be in accord with our definition) which agrees (too well?) with our value of 954 a.u. Note that the neglected vibrational contribution, to be discussed later, is comparatively very small for THG. Though there have been dc Kerr experiments for $H_2$,[35] we cannot make any comparisons since the experiment measures the difference in $\bar{\chi}_{\parallel}^{(3)}$ and $\bar{\chi}_{\perp}^{(3)}$ and we have not calculated the latter (it requires the $\gamma_{xxyy}$ component).

The most fruitful comparison is for the ESHG experiment: Following earlier work by Shelton and Buckingham[36] and by Ward and Miller,[37] Mizrahi and Shelton[15] have measured $\bar{\chi}_{\parallel}^{(3)}(-2\omega;0,\omega,\omega)$ as ratio for $H_2$ to He. In Table XI we give their absolute values (using the Sitz and Yaris[13] values for He) after the theoretical vibrational contribution has been extracted. The agreement for nonzero frequency values is very satisfying. There is, however, a significant difference between the values they obtain by linear extrapolation (in $\omega^2$) to $\omega=0$ (645 a.u.)

TABLE X. Comparison of dynamic hyperpolarizability components for $H_2$ (at $R=1.4a_0$) with those of Ref. 11, in atomic units.

| | | $\gamma(-\omega;\omega,\omega,-\omega)$ | | | $\gamma(-3\omega;\omega,\omega,\omega)$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| λ (Å) | Ref. | *xxxx* | *xxzz* | *zzzz* | *xxxx* | *xxzz* | *zzxx* | *zzzz* | $\bar{\gamma}(-3\omega;\omega,\omega,\omega)$ |
| 6943 | BP[a] | 626 | 218 | 765 | 780 | 273 | 282 | 976 | 833 |
| | JR[b] | 632 | 250 | 769 | 790 | 312 | 322 | 987 | 872 |
| 6328 | BP | 640 | 222 | 783 | 838 | 292 | 305 | 1056 | 897 |
| | JR | 648 | 256 | 787 | 853 | 338 | 352 | 1079 | 947 |
| 4880 | BP | 700 | 239 | 864 | 1145 | 395 | 428 | 1501 | 1240 |
| | JR | 708 | 282 | 872 | 1174 | 468 | 507 | 1557 | 1328 |

[a] This work.
[b] Values interpolated from the results of Ref. 11.

and our value (666 a.u.). We think that this is due to inadequacy in the extrapolation, which has to run from approximately 14 000 $cm^{-1}$ to 0 $cm^{-1}$. In fact, if we make a quadratic extrapolation (i.e., in $\omega^2$ and $\omega^4$) of the experimental data, we get 665, but we place no more credence in this value than the other one, since removal of some higher frequency points gives 705 a.u. The moral seems to be to compare pure experiment with pure theory, rather than try to meet on some middle ground ($\omega=0$). Mizrahi and Shelton[15] also give the ratios of the $H_2$ to $D_2$ $\bar{\chi}_{\parallel}^{(3)}$ values—they all hover around 1.03 as do the theoretical ratios which can be derived from the susceptibilities in Table VIII.

Several formulas for the dispersion properties (frequency dependence) of these processes have appeared in the literature, usually having a form which is linear in $\omega^2$. We find that a very satisfactory fit can be made to our results by a three-term expression in $\omega^2$ and $\omega^4$ and in Table XII we give the appropriate coefficients. The THG numbers give the poorest fit and we think that this is because the largest frequency we use leads to a value of $3\omega$ which is getting close to the lowest electronic excitation energy and consequent near resonance. Deletion of this point gives an improved fit. We should note that we could not satisfactorily fit the THG values of Jaszuński and Roos.[11] Further, it has been suggested[18] that all four processes could be unified by a *single* dispersion formula in $\omega_L^2$ where $\omega_L^2=\omega_\sigma^2+\omega_1^2+\omega_2^2+\omega_3^2$. This appears to be very nearly true: Taking the processes in the order dc Kerr (parallel component), DFWM, ESHG, THG, the ratio for $A$ (the constant) is predicted (see Table XII) and found to be 1:1:1:1; the ratio for $B$ (the coefficient of $\omega^2$ or $\lambda^{-2}$) is predicted to be 1:2:3:6 and found to be 1:2.0:2.9:4.2; the ratio for $C$ (the coefficient of $\omega^4$ or $\lambda^4$) is predicted to be 1:4:9:36 and found to be 1:4.5:10.6:69. That the THG results conform most poorly may be due to the inaccuracy of the results or the limitation of the hypothesis for this experiment. To find the same coefficients ($A$, $B$, and $C$) for $D_2$, one need simply divide the ones in Table XII by 1.03.

From Tables III–VI we are in a position to comment on the applicability of the Kleinman symmetry conjecture[17] to the microscopic hyperpolarizabilities.[16] For ESHG at 4880 Å the $\gamma_{xxzz}$, $\gamma_{xzzx}$, $\gamma_{zxxz}$, and $\gamma_{zzxx}$ values (at $R=1.4a_0$) vary by as much as 10% and to this extent the hypothesis is not valid at the microscopic level. Mizrahi and Shelton[16] have measured $\bar{\chi}_{ZZZZ}^{(3)}(-2\omega;0,\omega,\omega)/\bar{\chi}_{ZZXX}^{(3)}(-2\omega;0,\omega,\omega)$, which would be 3 if the "conjecture" applied, and find 2.86 from the raw data for $H_2$ (or 2.87 from the vibrationally corrected data)—that is to say, only a 4.5% discrepancy. It is clear that the value of this ratio is not a stringent enough test. We are unable to compute the ratio directly, since we have not calculated one of the components ($\gamma_{xxyy}$) which is needed for $\bar{\chi}_{ZZXX}^{(3)}$.

In Table XIII we show the purely vibrational contributions for $H_2$ and $D_2$, which were calculated with Eqs. (15)

TABLE XI. Comparison of theoretical and experimental ESHG susceptibilities: $\bar{\chi}_{\parallel}^{(3)}(-2\omega;0,\omega,\omega)$ in atomic units, for $H_2$ at 22 °C.

| λ (Å) | Theory[a] | Expt.[b] |
|---|---|---|
| ∞ | 666 | (645)[c] |
| 6943 | 792 | 805[d] |
| 6328 | 821 | 828 |
| 4880 | 959 | 973 |

[a] Present work and excluding purely vibrational contributions.
[b] From Ref. 15, using the $\chi_{H_2}/\chi_{He}$ (vibrationally corrected) values and $\chi_{He}=42.6\{1+[\omega/(58\,300\ cm^{-1})]^2\}$.
[c] This value comes from a linear extrapolation to $\omega=0$ of the experimental data; see text.
[d] An earlier experimental value (Ref. 37) is 777±10.

TABLE XII. Theoretical values of $A$, $B$, and $C$ in the expression $\bar{\chi}_{\parallel}^{(3)}=A+B/[\lambda\ (\text{Å})]^2+C/[\lambda\ (\text{Å})]^4$ for $H_2$ at $T=22\,°C$. (Values for $D_2$ can be found by dividing those in the table by 1.03.)

| | $A$ | $B/10^7$ | $C/10^{13}$ |
|---|---|---|---|
| $\bar{\chi}_{\parallel}^{(3)}(-\omega;0,0,\omega)$ | 666 | 175 | 435 |
| $\bar{\chi}_{\parallel}^{(3)}(-\omega;\omega,\omega,-\omega)$ | 666 | 342 | 1961 |
| $\bar{\chi}_{\parallel}^{(3)}(-2\omega;0,\omega,\omega)$ | 666 | 504 | 4610 |
| $\bar{\chi}_{\parallel}^{(3)}(-3\omega;\omega,\omega,\omega)$ | 666 | 736 | 29846 |

TABLE XIII. Vibrational components of the nonlinear susceptibilities in atomic units.

| | λ (Å) | ∞ | 6943 | 6328 | 4880 |
|---|---|---|---|---|---|
| $H_2$ | $\chi_{\parallel}^{v}(-\omega;0,0,\omega)$ | 184.24 | 50.00 | 52.08 | 56.03 |
| | $\chi_{\parallel}^{v}(-\omega;\omega,\omega,-\omega)$ | 184.24 | 121.47 | 121.70 | 122.15 |
| | $\chi_{\parallel}^{v}(-2\omega;0,\omega,\omega)$ | 184.24 | −12.73 | −10.42 | −6.01 |
| | $\chi_{\parallel}^{v}(-3\omega;\omega,\omega,\omega)$ | 184.24 | −3.98 | −3.30 | −1.95 |
| $D_2$ | $\chi_{\parallel}^{v}(-\omega;0,0,\omega)$ | 177.39 | 53.73 | 54.68 | 56.53 |
| | $\chi_{\parallel}^{v}(-\omega;\omega,\omega,-\omega)$ | 177.39 | 117.61 | 117.72 | 117.94 |
| | $\chi_{\parallel}^{v}(-2\omega;0,\omega,\omega)$ | 177.39 | −6.05 | −4.99 | −2.92 |
| | $\chi_{\parallel}^{v}(-3\omega;\omega,\omega,\omega)$ | 177.39 | −1.95 | −1.62 | −0.96 |

and (16), and the values for $\omega_k$, $\langle\alpha_{zz}\rangle_{0k}$, $\langle\alpha_{xx}\rangle_{0k}$ from Hunt *et al.*[38] The value for the static case for $H_2$, i.e., $\chi_{\parallel}^{v}(0)=184.74$, agrees with an independent calculation by Shelton,[28] who also finds a value of 182.8 a.u. when classical orientational averaging is *not* assumed—thus justifying this approximation which is embedded in Eq. (15). He also gives values at λ = 6328 Å which for DFWM, ESHG, and THG can be compared with ours. Bearing in mind that in Eq. (15) he sums only over the first excited vibrational state, his corrected numbers[39] are in good agreement with those in Table XIII. At the usual experimental frequencies it is clear that $\chi_{\parallel}^{v}$ is important for DFWM and may also be important for the dc Kerr experiment (we cannot tell since we have not computed $\chi_{\perp}^{v}$) but is of much less significance for ESHG and THG—though still to be considered if any accuracy better than 1% is desired.

## IV. CONCLUSIONS

The first, and perhaps most important, conclusion is that it appears to be possible to make accurate calculations of the third-order susceptibilities for small molecules which can be used as a "benchmark" or standardization of the experimental results. At experimental frequencies ($\omega\neq0$) our results are in excellent agreement with recent ESHG experiments. It is cautioned, however, that such experimental values should not be extrapolated to zero frequency if their precision is to be maintained. The conjecture of Kleinman symmetry on the microscopic level appears to be only partially valid. Expressions for dispersion as short polynomials in $\omega^2$ work well except for THG. Vibrational contributions (over and above conventional vibrational averaging) should always be investigated (it is not difficult), especially when 1% accuracy is

TABLE XIV. Values of *a*,*b*,*c*,*d* for Eq. (17) in atomic units, the power of ten in square brackets.

| | λ (Å) | *a* | *b* | *c* | *d* |
|---|---|---|---|---|---|
| $\bar{\gamma}(-\omega;0,0,\omega)$ | ∞ | 7.497[1] | −1.141[2] | 2.557[2] | 6.607[1] |
| | 6943 | 7.007[1] | −8.788[1] | 2.224[2] | 8.981[1] |
| | 6328 | 7.125[1] | −9.094[1] | 2.232[2] | 9.305[1] |
| | 4880 | 7.056[1] | −8.029[1] | 2.015[2] | 1.137[2] |
| $\bar{\gamma}(-\omega;\omega,\omega,-\omega)$ | ∞ | 7.497[1] | −1.141[2] | 2.557[2] | 6.607[1] |
| | 6943 | 6.986[1] | −7.813[1] | 2.006[2] | 1.132[2] |
| | 6328 | 6.810[1] | −6.748[1] | 1.845[2] | 1.254[2] |
| | 4880 | 5.615[1] | −2.764[0] | 9.253[1] | 1.864[2] |
| $\bar{\gamma}(-2\omega;0,\omega,\omega)$ | ∞ | 7.497[1] | −1.141[2] | 2.557[2] | 6.607[1] |
| | 6943 | 6.723[1] | −5.732[1] | 1.643[2] | 1.433[2] |
| | 6328 | 5.767[1] | −1.391[1] | 1.120[2] | 1.707[2] |
| | 4880 | 2.671[1] | 1.438[2] | −1.099[2] | 3.008[2] |
| $\bar{\gamma}(-3\omega;\omega,\omega,\omega)$ | ∞ | 7.497[1] | −1.141[2] | 2.557[2] | 6.607[1] |
| | 6943 | 2.756[1] | 1.401[2] | −1.064[2] | 2.983[2] |
| | 6328 | −3.658[0] | 2.877[2] | −3.043[2] | 3.989[2] |
| | 4880 | −4.247[2] | 2.146[3] | −2.649[3] | 1.403[3] |

demanded. Further work along the lines of this article is underway for He and $H_2^+$.

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## APPENDIX

The parameters for Eq. (17) are listed in Table XIV.

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