

Measurements of second- and third-order nonlinear polarizabilities for HF and HCl

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Measurements of second- and third-order nonlinear polarizabilities (hyperpolarizabilities) for HF and HCl using dc electric-field-induced second-harmonic generation are presented: $\chi_{\parallel}^{(3)}(\text{HF}) = 70(10) \times 10^{-39}$ esu/mol, $\chi_{\parallel}^{(2)}(\text{HF}) = -4.70(41) \times 10^{-32}$ esu/mol, $\chi_{\parallel}^{(3)}(\text{HCl}) = 347(15) \times 10^{-39}$ esu/mol, $\chi_{\parallel}^{(2)}(\text{HCl}) = -4.22(50) \times 10^{-32}$ esu/mol. In the case of HF this allows a critical comparison with theory. HF has fewer electrons than any polar molecule previously studied experimentally and the small size of HF has made it an attractive candidate for theoretical investigation. Christiansen and McCullough have used numerical Hartree-Fock techniques to establish generally accepted criteria for basis set selection; and Bartlett and Purvis have applied to HF the most elaborate technique applied so far to the calculation of any molecular hyperpolarizability (CHF SDQ-MBPT[4]). Experimental corrections and uncertainties are carefully considered as are several other factors relevant to a comparison of these experimental and theoretical data. The theoretical results are about a factor of 2 smaller than the experimental data and none of the factors considered seems to offer a resolution of this discrepancy.

I. INTRODUCTION

We wish to report measurements of second- and third-order electric polarizabilities (hyperpolarizabilities) for HF and HCl molecules, using dc electric-field-induced second-harmonic generation (dcSHG).

Experimental and theoretical values for hyperpolarizabilities¹ have been available for fifteen years and although the sophistication of the theoretical techniques has increased substantially during this period, the agreement between experiment and theory is still inadequate. HF is of particular importance, being smaller (in the sense of fewer electrons) than any polar molecule investigated experimentally until now. In addition to improving the chance of success of any calculation, the small number of electrons in HF makes numerical techniques available which would not be practicable for larger molecules.

Measurements are described in Sec. II. In Sec. III, theoretical work is reviewed briefly, particularly the hyperpolarizability calculations for HF by Bartlett and Purvis.² Various additional factors are examined which need to be included when theoretical and experimental results are compared. Theoretical results are found to be about a factor of 2 smaller than the experimental data, a discrepancy which we find somewhat surprising considering the sophistication of the calculation and the small number of electrons in HF.

II. EXPERIMENTAL

Notation and experimental arrangement are similar to those of Refs. 3-5 and are reviewed briefly here.

Molecules in a gas subjected to a dc electric field

and an optical electric field at frequency ω develop a dipole moment at the second-harmonic frequency 2ω . The average induced dipole moment amplitude per molecule $\bar{p}^{2\omega}$ may be written

$$\bar{p}^{2\omega} = \frac{3}{2} \chi_{\parallel}^e(-2\omega; 0, \omega, \omega) E^0 (E^\omega)^2, \quad (1)$$

where $\chi_{\parallel}^e(-2\omega; 0, \omega, \omega)$ is an effective molecular hyperpolarizability with \parallel indicating that all fields are in the same direction, and E^0 and E^ω are field amplitudes at frequencies indicated by superscripts. The effective hyperpolarizability includes, in addition to the intrinsic molecular third-order polarizability, a contribution from the second-order polarizability. This additional term is non-zero in the case of molecules with permanent electric dipole moments (μ) which undergo temperature-dependent partial alignment by the dc field. The two contributions can be written explicitly:

$$\begin{aligned} \chi_{\parallel}^e(-2\omega; 0, \omega, \omega) \\ = \chi_{\parallel}^{(3)}(-2\omega; 0, \omega, \omega) + (\mu/9kT) \chi_{\parallel}^{(2)}(-2\omega; \omega, \omega). \end{aligned} \quad (2)$$

A quantum correction to the alignment term, and the relationship of the laboratory-frame, average hyperpolarizabilities considered here to the molecular-frame hyperpolarizabilities will be discussed later. Conventions used here in the definitions of hyperpolarizabilities are discussed in Ref. 6. In particular, the factor $\frac{3}{2}$ in Eq. (1) ensures a simple relationship to static polarizabilities:

$$\text{Limit}_{\omega \rightarrow 0} \chi(-2\omega; \omega, \omega) = \chi(0; 0, 0),$$

$$\text{Limit}_{\omega \rightarrow 0} \chi(-2\omega; 0, \omega, \omega) = \chi(0; 0, 0, 0). \quad (3)$$

The gas under observation is contained in a cell at density ρ . The optical field is generated by a 1 MW Q -switched ruby laser focused into the gas, and the dc field is provided by cylindrical electrodes located in the plane of the focus. The equivalent line-electrode separation is d and the potential difference is V_0 . The dipoles $\bar{p}^{2\omega}$ generate second-harmonic radiation which is detected by a photomultiplier and associated electronics to produce a voltage V_S proportional to the second-harmonic intensity. A portion of the ruby laser beam is reflected through a quartz crystal, and the second harmonic so generated is similarly detected to yield a voltage V_M which serves as a monitor of fundamental beam intensity. A quantity S (referred to here as the "signal") is then defined in terms of these measured quantities

$$S \equiv V_S / (V_M V_0^2). \quad (4)$$

It can be shown⁷ that in this experimental geometry,

$$S = \text{const} \times \Gamma(\rho/\rho_0) \times |\chi_{\parallel}^e / \Delta k_0|^2, \quad (5)$$

where the constant is independent of the gas investigated, and frequency labels have been omitted for brevity. $\Gamma(\rho/\rho_0)$ is given by

$$\Gamma(\rho/\rho_0) = \left[\frac{\rho}{\rho_0} \exp\left(\frac{\rho_0 - \rho}{\rho_0}\right) \right]^2 \quad (6)$$

and ρ_0 is the optimum density

$$\rho_0 = \frac{2}{d|\Delta k_0|}. \quad (7)$$

Δk_0 is a measure of the optical dispersion of the gas and is related to the wave vectors for the fundamental (k_0^0) and harmonic ($k_0^{2\omega}$) by

$$\Delta k_0 = 2k_0^{\omega} - k_0^{2\omega}. \quad (8)$$

The subscripts zero here indicate quantities evaluated for a gas at a molecular number density of Loschmidt's number per cm^3 .

The data are derived from the results of several different experiments which have been described previously.⁴ A brief review and details specific to the current experiment will be given here.

A. $|\chi_{\parallel}^e(T)|$

The gas handling apparatus was largely constructed from monel with copper or nickel electrodes. Sapphire windows and Kalrez O-rings were used with HF, quartz windows and Viton O-rings with HCl. HF and HCl were transferred from the optical cell to a monel reservoir by cooling the reservoir with liquid nitrogen. This procedure allowed hydrogen impurity to be pumped away at each transfer. Pressure was measured with a corrosion-resistant, bakable Datametrics capacitance manometer.

The signal S was measured for the gas of interest and a comparison gas alternately, keeping temperature and ρ/ρ_0 unchanged but adjusting V_0 for each gas to get comparable signals. Then from Eq. (5),

$$|\chi_{\parallel}^e(T)| = \sqrt{\frac{S(T)}{S'(T)}} \times \left| \frac{\Delta k_0}{\Delta k_0'} \right| \times |\chi_{\parallel}^e(T)|, \quad (9)$$

where primed quantities refer to comparison gases: CF_4 for HF and CH_4 for HCl.

Setting $\rho/\rho_0 = 1$ optimizes the signal and minimizes sensitivity to the value of ρ/ρ_0 . For HF, however, association is a factor to be considered. To keep the dimer fraction small (<1.2%) it was necessary to reduce the density to $\rho/\rho_0 = 1/4$. Measurements with both HF and the comparison gas CF_4 were carried out under these conditions, whereas HCl and CH_4 were both studied at $\rho/\rho_0 = 1$.

Previous measurements^{3,4} have related comparison gas hyperpolarizabilities to that of helium, for which we use a value calculated by Sitz and Yaris⁸ and thought to be good to 1%. Alternative normalization to the experimental Kerr polarizability for He⁹ and using a theoretical ratio⁸ of the dcSHG to Kerr polarizability would increase the magnitude of our results by 23%.

B. Sign of χ_{\parallel}^e

The relative signs of χ_{\parallel}^e for two gases can be determined by measuring $|\chi_{\parallel}^e|$ for mixtures of the gases.¹⁰ HF- CF_4 and HCl- CH_4 mixtures were studied here. Absolute signs are determined through a chain of previous comparisons either to helium^{3,4} where the calculated value⁸ is positive, or equivalently, to argon¹¹ where it can be assumed that the sign of the dcSHG polarizability is the same as the sign of the measured Kerr polarizability.⁹

C. Δk_0

The wave vector mismatch Δk_0 , defined by Eq. (8), is required both to determine ρ_0 from Eq. (7) so that ρ/ρ_0 can be set equivalently for experimental and comparison gas pairs, and also to use in Eq. (9) to extract values for $|\chi_{\parallel}^e(T)|$. Δk_0 is determined¹² by studying interference between harmonic generated in two quartz plates as the density of experimental gas is changed in a cell located between the plates. Deviations from ideal gas behavior are taken into account in determining gas density.

Experimental data for Δk_0 is shown in Table I. For HCl our measured value of Δk_0 is in good agreement with that derived from refractive index data.¹⁶ For HF, Δk_0 represents the only refractive index dispersion data available to our knowledge for the gas although data is available for liquid HF.¹⁷

D. $\chi_{\parallel}^{(2)}$ and $\chi_{\parallel}^{(3)}$

$\chi_{\parallel}^e(T)$ was measured at a particular temperature by alternating 12 subruns of 40 laser shots each with experimental and comparison gases. Data taken over a range of temperatures is shown in Fig. 1 plotted vs T^{-1} . The error flags indicate standard deviations and are dominated by photon statistics. Values of a number of experimental parameters are shown in Table I. $\chi_{\parallel}^{(2)}$ and $\chi_{\parallel}^{(3)}$ are derived from the slope and intercept of Fig. 1 using Eq. (2). The

TABLE I. Experimental results for HF and HCl: Δk_0 , $\chi_{||}^{(2)}$ and $\chi_{||}^{(3)}$, including all corrections and uncertainties discussed in Sec. II of the text. Experimental parameters used for these measurements are shown, together with relevant data from the literature.

	E_{max}^0 (esu)	T (K)	ρ (amagat)	ρ/ρ_0	$-\Delta k_0$ (cm^{-1})	μ^a (Debye)	$10^{32} \times \chi_{ }^{(2)}$ (esu)	$10^{39} \times \chi_{ }^{(3)}$ (esu)
H^+F^-	17	373-494	0.720	1/4	0.880 (16) ^b	1.82 (1)	-4.70 (41)	70 (10)
CF_4	29	373-494	0.308	1/4	2.03 (5) ^c	91 (3) ^c
H^+Cl^-	23	295-399	0.640	1	4.58 (7) ^d	1.08 (2)	-4.22 (50)	347 (15)
CH_4	17	295-399	0.716	1	4.08 (4) ^e	263 (3) ^e

^a Permanent dipole moments from Ref. 13.

^b Density corrected using association data from Ref. 14.

^c Reference 3.

^d Using virial data from Ref. 15.

^e Reference 4.

sign of $\mu\chi_{||}^{(2)}$ is unambiguously determined to be negative from the negative slope of the data in Fig. 1 for both HF and HCl. We further assign to $\chi_{||}^{(2)}$ the same negative sign which is equivalent to choosing a molecular z axis with the same direction and sense as the molecular permanent dipole moment. Results for $\chi_{||}^{(2)}$ and $\chi_{||}^{(3)}$ shown in Table I include uncertainties routinely propagated from various experimental parameters ($\pm 1\%$ from V_0 , $\pm 3\%$ from ρ/ρ_0 in the case of HF, and so on) as well as a correction and uncertainties from additional sources discussed next.

E. A correction and additional sources of uncertainty

Quantum corrections to the temperature-dependent alignment term in Eq. (2) have been discussed by Buckingham and Orr¹⁸ who give

$$\mu\chi_{||}^{(2)} \rightarrow \mu\chi_{||}^{(2)}(1 - hcB_0/3kT \dots), \quad (10)$$

where the rotational constants B_0 (Ref. 19) are 20.96 cm^{-1} (HF) and 10.59 cm^{-1} (HCl). The T^{-2} temperature dependence of this correction necessitates adjustments to values deduced from both the slope and intercept of Fig. 1: $\chi_{||}^{(2)}$ (HF), +4.6%; $\chi_{||}^{(3)}$ (HF), +5.5%; $\chi_{||}^{(2)}$ (HCl), +3.0%; and $\chi_{||}^{(3)}$ (HCl), +0.5%.

Special consideration must be given to the effects of association in HF.¹⁴ At the density used in these experiments, the dimer fraction varies from 0.2% at 494 K to

1.2% at 373 K. Association has been taken into account in determining number densities (specifically, the number of HF units per cm^3) from pressure and density data in both $|\chi_{||}^{(2)}(T)|$ and Δk_0 experiments. Association constants were determined using the method of Maclean *et al.*¹⁴ In addition to this, association can change molecular electrical properties both by correlating the orientation of the associating molecules, and, by keeping them relatively close together, accentuate intermolecular interactions. We believe the effects of interaction will be small. Orientational correlation should have little effect on $\chi_{||}^{(3)}$ and Δk_0 , but can have a substantial effect on $\mu\chi_{||}^{(2)}$. For relative orientations of molecular axes of 0° , 90° , 180° for an associated pair of molecules, the value of $\mu\chi_{||}^{(2)}$ per associated molecule will be 0, 1, 2 times that of an unassociated molecule. Noting the temperature dependence of the dimer fraction, this leads to a worst-case error in extracting $\chi_{||}^{(2)}$ and $\chi_{||}^{(3)}$ from Fig. 1 of $\pm 8\%$ and $\pm 14\%$, respectively. However, recent studies²⁰ show that the relative orientation of associated molecules is close to 90° in which case no error from orientational correlation arises. To account both for deviations from 90° relative orientation and for interactions between associated molecules, we include uncertainties 4% in $\chi_{||}^{(2)}$ and 7% in $\chi_{||}^{(3)}$.

Gases supplied by Matheson in lecture bottles have been used in this work. Quoted minimum purity levels are HF (99.9%), CF_4 (99.7%), HCl (99.0%), and CH_4 (99.0%). In addition, some hydrogen is evolved by HF and HCl by interaction with the metal apparatus and lecture bottle. The hydrogen is pumped off after freezing the experimental gas at each transfer. The most significant impurities in each case are residual hydrogen (estimated at $< 0.8\%$) in HF; chlorinated ethanes in HCl; and there are no important impurities in CF_4 or CH_4 . Resulting uncertainties are estimated as: $\chi_{||}^{(2)}$ (HF), $\pm 1\%$; $\chi_{||}^{(3)}$ (HF), $\pm 0.5\%$; $\chi_{||}^{(2)}$ (HCl), $\pm 2.0\%$; $\chi_{||}^{(3)}$ (HCl), $< \pm 0.1\%$.

Values of $\chi_{||}^{(2)}(-2\omega; \omega, \omega)$ and $\chi_{||}^{(3)}(-2\omega; 0, \omega, \omega)$ in Table I include all corrections and uncertainty contributions discussed here. The alternative normalization discussed in Sec. II A above would increase the magnitudes of these results by 23%.

III. THEORETICAL

There are a number of calculations in the literature of hyperpolarizabilities for small molecules at the

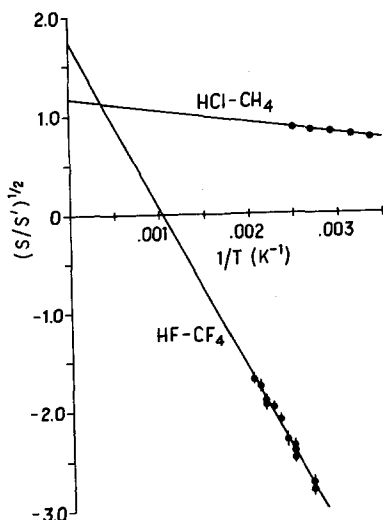


FIG. 1. Square root of the ratio of signals as a function of inverse temperature with sign determined by the experimental sign of $\chi_{||}^{(2)}$. The ordinate is proportional to $\chi_{||}^{(2)}$ [see Eq. (9)]. Error flags are standard deviations over the set (~ 500) of laser shots from which a given data point is derived. In the case of HCl, error flags are smaller than the data point symbols.

uncoupled Hartree–Fock,^{21–23} coupled Hartree–Fock (CHF)^{24–26} and correlated^{2,27,28} levels. These are all static treatments and attempts at a frequency-dependent calculation²⁹ have been rare. For HF particularly there is an extensive body of theoretical work^{30–33} on the permanent dipole moment and linear polarizability α , and some corresponding work on HCl.^{32,34} Calculations of hyperpolarizabilities exist for both HF^{2,22,23,25,26} and HCl.²³

Christiansen and McCullough^{26,35} (CM) have investigated the problem of the selection of suitable basis sets for hyperpolarizability calculations by comparing results obtained with various basis sets against a numerical CHF calculation. Axial components of the molecular second-order (β_{zzz}) and third-order (γ_{zzzz}) polarizabilities³⁶ were calculated for HF. Residual discrepancies of 8% for β and 3% for γ between results using the best basis set and the numerical calculation remain unexplained. This recipe for basis set construction has been widely used in subsequent calculations without limitation to $zz \cdots$ components or to the HF molecule. Bartlett and Purvis² have carried out a more sophisticated calculation for most components of β and γ in HF, including the effects of electron correlation. They used a modified CM basis set since difficulties arose in using the original CM basis set for nonaxial components. The selected basis set showed residual discrepancies with respect to the numerical CHF calculation of 2% for β and 12% for γ . Electron correlations were included using fourth-order many body perturbation theory, including all single, double, and quadruple excitations (SDQ-MBPT[4]). Correlation contributions are significant, changing β by 22% and γ by 28%.

The only hyperpolarizability calculation for HCl²³ was an early attempt and only axial components β_{zzz} and γ_{zzzz} were computed. The method applied by Bartlett and Purvis² to HF could be extended to HCl with some additional approximation in the treatment of inner electrons.³⁷ We now concentrate on HF exclusively.

The relations between static $\chi_{||}^{(2)}$ and β , and static $\chi_{||}^{(3)}$ and γ involve taking an orientational average, noting the $C_{\infty v}$ symmetry of the HF molecule, including conventional factors³⁸ from the definitions of β and γ , and unit conversions. The relations are

$$\chi_{||}^{(2)} = \frac{1}{2} \times \frac{2}{3} \{ \beta_{zzz} + 2\beta_{zxx} \} \times 8.639 \times 10^{-33} \text{ esu/a.u.} \quad (11)$$

and

$$\chi_{||}^{(3)} = \frac{1}{6} \times \left\{ \frac{1}{5} \gamma_{zzzz} + \frac{4}{3} \gamma_{yyzz} + \frac{8}{15} \gamma_{yyyy} \right\} \times 5.037 \times 10^{-40} \text{ esu/a.u.} \quad (12)$$

Since γ_{yyyy} has not been calculated^{38(a)} we use an estimate based on the assumed approximate isotropy of γ

$$\gamma_{yyyy} \approx \frac{1}{2} \times \{ \gamma_{zzzz} + 3\gamma_{yyzz} \}. \quad (13)$$

The sign of $\chi_{||}^{(2)}$ and β depend on the molecular coordinate system and, in particular, on the sense of the molecular z axis. In both the present experimental work and in Ref. 2 this is taken to be from F^- to H^+ .

The results from Eq. (11) and Eqs. (12 and 13) are shown, without further modification, in Table II. Several additional considerations which should be taken into

TABLE II. Comparison of experimental and theoretical values for the second- and third-order nonlinear polarizabilities for HF. Experimental values include corrections and uncertainty contributions discussed in the text. An alternative normalization would increase the experimental magnitudes shown by 23%. Theoretical values come via Eqs. (11)–(13). Estimated corrections ($\times 1.14$) are not included, nor is the vibrational correction which might be expected to be of the order of 10%.

	$10^{32} \times \chi_{ }^{(2)}$ (esu)	$10^{39} \times \chi_{ }^{(3)}$ (esu)
Experiment	–4.70 (41)	70 (10)
Theory ^a	–2.83	35

^a Reference 2.

account in predicting the measured nonlinear polarizabilities are discussed below.

A. Dispersion

Dispersion of hyperpolarizabilities can be calculated approximately using expressions³⁹ analogous to the Sellmeier equation often used to represent dispersion in the linear case. Using an estimate of a characteristic frequency for HF (4×10^{15} Hz) from refractive index data for liquid HF¹⁷ yields

$$\chi(-2\omega; 0, \omega, \omega) \approx \chi(0; 0, 0, 0) \times [1 + 14\%]. \quad (14)$$

This estimate for the dispersion of $\chi_{||}^{(3)}$ should also serve as a conservative limit on the dispersion for $\chi_{||}^{(2)}$.

B. Internuclear separation: the vibrational correction

Molecular electric properties are calculated at a fixed value of the internuclear separation, whereas the measured property is an average over the vibrational motion.^{28,30,33,35} In addition, centrifugal distortion should be included for excited rotational states.^{28,33} Werner and Meyer³⁰ calculate a 2% vibrational correction to the average static linear polarizability of HF and Purvis and Bartlett²⁸ calculate an 11% correction to β for H₂O. Amos,³³ however, has expressed doubts about the adequacy of Hartree–Fock wave functions for evaluating vibrational corrections. In any case, vibrational corrections to β and γ have not been calculated for HF, but corrections to the results of Bartlett and Purvis² (calculated at the equilibrium separation) on the order of 10% can be anticipated.

It is worth noting that orientational contributions to dcSHG, the Kerr effect, and so on, involve products such as $\mu\beta$. It seems to have escaped mention that, in principle, the vibrational correction should be applied to the *product* and not to each factor individually.

C. Vibrational contributions

The vibrational contributions considered here^{40,41} are analogous to the atomic polarization contribution to the static linear polarizability and are completely neglected in a calculation done at fixed internuclear separation. In a time-dependent perturbation picture of the hyperpolarizabilities, these terms appear when a vibrationally excited member of the ground electronic state serves as an intermediate state, and the corresponding perturbation arises from a subset of the applied fields with frequencies

summing to zero. Such contributions are absent for $\chi^{(2)}(-2\omega; \omega, \omega)$. Detailed investigation⁴¹ of $\chi^{(3)}$ in a number of molecules indicates that vibrational contributions are small (<1%) for dcSHG, particularly for molecules such as HF (and HCl) with large vibrational frequencies.

IV. CONCLUSION

Experimental values for $\chi_{||}^{(2)}$ and $\chi_{||}^{(3)}$ including all corrections and uncertainty contributions discussed in Sec. II are shown in Table II together with static theoretical values obtained using Eqs. (11) and (12). The agreement is poor, with the theoretical values being about a factor of 2 smaller than the experimental values. This is particularly disturbing for a molecule with only ten electrons and for which a sophisticated theoretical treatment is available. It is also disturbing that such a large discrepancy should arise for the molecule whose study has established basis set selection practice for polarizability and hyperpolarizability calculations.

It is interesting to compare typical discrepancies between theory and experiment for μ , α ,³⁰ β , and γ :

$$\mu(1.5\%), \quad \alpha(5\%), \quad \beta(100\%), \quad \gamma(100\%),$$

but it should be noted that the sequence appears less anomalous if *anisotropic* properties are considered:

$$\mu(1.5\%), \quad \Delta\alpha(5-15\%), \quad \beta(100\%).$$

In any case, it is appropriate to speculate on possible sources of the discrepancy:

Vibrational corrections could account for a substantial fraction of the discrepancy and this possibility can be resolved when appropriate derivatives with respect to internuclear separation become available.

Dispersion has been crudely estimated to be only a 14% correction. While it would be surprising if this were a substantial underestimate, a better evaluation would be useful. It would be unrealistic to anticipate soon a fully frequency-dependent calculation comparable in sophistication to the current static calculation, but perhaps frequency dependent calculations²⁹ can be developed which will properly reproduce experimental dispersion without necessarily reducing to the correct static limit.

Although the CM criteria for basis set selection represent a substantial advance, the basis set used by Bartlett and Purvis² is still significantly incomplete since it yields a CHF value for γ_{zzzz} which differs by 12% from the numerical CHF value.

Diercksen *et al.*⁴² have discussed the role of approximations in the SDQ-MBPT [4] scheme. Specifically, they find that the omitted triple excitations can make a significant contribution.

Use of the alternate normalization discussed in Sec. II for the experimental results would *increase* the discrepancy.

It may be hoped that the resolution of this discrepancy for HF will allow progress toward a detailed understanding of hyperpolarizabilities in larger molecules.

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