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Constrained anisotropic dipole oscillator strength distribution techniques, and reliable results for anisotropic and isotropic dipole molecular properties, with applications to H_2 and N_2*

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Summary. Constrained anisotropic dipole oscillator strength distribution techniques are discussed and applied to obtain reliable results for a wide variety of the anisotropic and isotropic dipole properties of H_2 and N_2. These include the dipole oscillator strength sums S_k, $k = 2, 1, -1/2(-1/2) -2, -3, -4, \ldots$, the logarithmic dipole sums L_k and mean excitation energies I_k, $k = 2(-1)-2$, and, as a function of wavelength, the dynamic polarizability and the associated anisotropy, the total depolarization ratio, the Rayleigh scattering cross section, and the Verdet constant. The anisotropic components of the DOSD for a molecule are obtained from a given recommended isotropic DOSD by using a constrained least squares procedure and a series of known anisotropic constraints. Assuming that sufficient input is available, the constrained DOSD approach used in this paper is the only available method for the reliable evaluation of *all* the relevant anisotropic and isotropic dipole properties for a wide variety of atoms and molecules.

Key words: DOSD – Anisotropic constraints – Dipole properties

1. Introduction

The construction of globally reliable isotropic molecular dipole oscillator strength distributions (DOSDs), and their use in evaluating accurate results for a wide variety of isotropic dipole molecular properties and in studying the additivity of these properties, has been discussed in detail in the literature [1–7]. Assuming the required input is available, this constrained DOSD approach, from a practical viewpoint, is the only available method for the accurate evaluation of *all* the relevant isotropic dipole properties for all but the smallest molecules. To date some forty atoms and molecules have been studied using constrained DOSD

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*** On leave from Department of Physics, Meerut University, Meerut, India techniques (H, Li, N, O, H_2, N_2, O_2, NO, NH_3, H_2O, N_2O, CH_4, CO, CO_2, n-C_sH_{2s+2} for $2 \leqslant s \leqslant 8$, ethylene, propene, 1-butene, methanol, ethanol, n-propanol, OCS, CS_2, SO_2, Ne, Ar, Kr, Xe, HF, HCl, HBr, SF_6, H_2S, acetylene and benzene [1, 8–12, 2, 13, 14]).

Part of the purpose of this paper is to discuss the reliable evaluation of anisotropic dipole molecular properties through an extension of the constrained isotropic DOSD approach. The extension is illustrated by applications to the properties of H_2 and N_2 and included in the discussion is a comparison of our results with a wide selection of available experimental and theoretical literature values.

The relationship between the anisotropic components of a molecular DOSD and the anisotropic dipole properties of a given molecule, and their relationship with the corresponding isotropic DOSD and properties, are reviewed in Sect. 2 for linear molecules (the explicit examples considered later are diatomic molecules (H_2, N_2) in Σ ground states). The properties considered in this paper are the dipole oscillator strength sums S_k, $k = 2, 1, -1/2(-1/2) -2, -3, -4, \ldots$, the logarithmic dipole sums L_k and mean excitation energies I_k, $k = 2(-1)-2$, and, as a function of wavelength, the dynamic polarizability and the associated anisotropy, the total depolarization ratio, the Rayleigh scattering cross section, and the Verdet constant, for the given molecule. In general both the ($\perp$, and $\|$) anisotropic components, and the isotropic results, for the properties are considered.

The constrained anisotropic DOSD approach is discussed briefly in Sect. 3; more details, with an application to the evaluation of the anisotropic dipole dispersion energies for interactions involving H_2, N_2 and rare gases, can be found in a recent paper [15]. The anisotropic DOSD for a given molecule is obtained, from the previously determined recommended isotropic DOSD, by using a constrained least squares procedure and a series of anisotropic constraints; the constraints used for H_2 and N_2 are summarized in Sect. 3.2. The results for the anisotropic components, and for the isotropic values, for all the dipole properties of H_2 and N_2 mentioned in the last paragraph, are presented in Sect. 4 where they are compared with selected experimental and theoretical literature results. A brief discussion of the importance of this paper, including an assessment of the reliability of the results for the dipole properties of H_2 and N_2, is given in Sect. 5. The relevance of some of the dipole properties is also discussed briefly in this section (see also Sect. 2). Results for the anisotropic dipole properties can be used to discuss the anisotropy, as a function of property and molecule, and this is illustrated by an example relative to the stopping and straggling of fast charged particles in H_2 and N_2. The (potential) use of reliable *ab initio* results for the anisotropic components of the dipole properties S_2, S_1 and S_{-1}, all of which can be evaluated using only ground-state molecular wavefunctions, as anisotropic constraints is also stressed.

Dedication. This paper is dedicated to the memory of Joe Hirschfelder, a superb scientist, a fine teacher, and a good friend.

2. Relationship between anisotropic DOSDs and dipole properties

A wide variety of important anisotropic dipole properties for a linear molecule can be evaluated provided reliable perpendicular ($\perp$-DOSD) and parallel

($\|$-DOSD) dipole oscillator strength distributions are available for the molecule of interest [7, 15–19]. These include the perpendicular ($\zeta = \perp$) and parallel ($\zeta = \|$) components of the dipole oscillator strength sums S_k and L_k, the related mean excitation energies I^ζ_k, and the dynamic polarizabilities $\alpha^\zeta(\epsilon)$ of the molecule, which are defined by:

$$S^\zeta_k = \int_{E_\zeta}^{\infty} dE(E/E_H)^k(df^\zeta/dE) \tag{1}$$

$$L^\zeta_k = \int_{E_\zeta}^{\infty} dE(E/E_H)^k \ln(E/E_H)(df^\zeta/dE) \tag{2}$$

$$I^\zeta_k = E_H \exp(L^\zeta_k/S^\zeta_k) \tag{3}$$

where $k = 2.5, 2, 1, 0, -1, \ldots$ and

$$\alpha^\zeta(\epsilon) = E_H^2 a_0^3 \int_{E_\zeta}^{\infty} dE(df^\zeta/dE)(E^2 - \epsilon^2)^{-1} \tag{4}$$

Here the E_ζ are the electronic absorption thresholds, and the (df^ζ/dE) are the differential dipole oscillator strengths at photon energy E, for the perpendicular ($\zeta = \perp$) and parallel ($\zeta = \|$) dipole-allowed transitions of the molecules of interest, E_H is the Hartree of energy, a_0 is the Bohr radius and $\epsilon = hc/\lambda$ is the energy associated with a photon of wavelength λ. For a ground-state molecule in a Σ state, $\|$ and $\perp$ transitions correspond to $\Sigma \rightarrow \Sigma$ and $\Sigma \rightarrow \Pi$ transitions, respectively. The relation between the anisotropic components of a dipole property for a linear molecule, and the rotationally averaged or isotropic value of the property P (for L or S), is given by:

$$P = [2P^\perp + P^\|]/3 \tag{5}$$

These properties find application in many areas of research. For example $\alpha^\zeta = a_0^3 S^\zeta_{-2} = \alpha^\zeta(\epsilon \rightarrow 0)$ is the ζ-component of the static dipole polarizability. The S^ζ_k, $k = -4, -6, -8, \ldots$, are other moments of the $\|$- and $\perp$-DOSDs that occur in the Cauchy expansion of the components of the frequency dependent or dynamic polarizability, or the molar refractivity ($R^\zeta_\lambda = (4\pi/3)N\alpha^\zeta(\epsilon)$ where N is Avogadro's number), of the molecule [16, 19–21]. Also the (I^ζ_1, S^ζ_1), I^ζ_0 and $(I^\zeta_{-1}, S^\zeta_{-1})$ are important for determining the straggling, stopping, and total inelastic scattering cross sections, respectively, for fast charged particles in matter, while the charge densities at the nuclei and Lamb shifts are related to the S^ζ_2 and I^ζ_2, respectively [1, 4, 22–26]. The anisotropy of a given molecular property can be discussed by comparing P, $P^\perp$ and $P^\|$.

There are several interesting dipole molecular properties that are related to the isotropic dynamic polarizability $\alpha(\epsilon)$, and to its parallel and perpendicular components defined by Eq. (4). The total depolarization ratio for vertically polarized incident light, for a given molecule, is given by [16, 21, 27]:

$$\varrho_v^T(\epsilon) = 3\gamma^2(\epsilon)/(45\alpha^2(\epsilon) + 4\gamma^2(\epsilon)) \tag{6}$$

where the anisotropy of the dynamic polarizability $\gamma(\epsilon)$ is defined by:

$$\gamma(\epsilon) = \alpha^\|(\epsilon) - \alpha^\perp(\epsilon) \tag{7}$$

The Rayleigh scattering cross section is given by [7, 16, 28]:

$$Q_{\mathrm{Ray}}(\epsilon) = \frac{128\pi^5}{9\lambda^4}[3\alpha^2(\epsilon) + \tfrac{2}{3}\gamma^2(\epsilon)] \tag{8}$$

Isotropic molecular dipole properties can be evaluated directly from the isotropic dipole oscillator strength distribution (DOSD) for a molecule. For example:

$$S_k = \int_{E_0}^{\infty} dE(E/E_H)^k(df/dE) \tag{9}$$

$$L_k = \int_{E_0}^{\infty} dE(E/E_H)^k \ln(E/E_H)(df/dE) \tag{10}$$

$$I_k = E_H \exp(L_k/S_k) \tag{11}$$

and

$$\alpha(\epsilon) = E_H^2 a_0^3 \int_{E_0}^{\infty} dE(df/dE)(E^2 - \epsilon^2)^{-1} \tag{12}$$

where E_0 is the electronic absorption threshold for the molecule and (df/dE) is the isotropic differential dipole oscillator strength at photon energy E:

$$df/dE = [2(df^{\perp}/dE) + (df^{\parallel}/dE)]/3 \tag{13}$$

Two other isotropic properties, related to $\alpha(\epsilon)$, are of particular interest in what follows. The isotropic molar refractivity, R_λ, relates the refractive index of the molecule to the isotropic dipole polarizability:

$$R_\lambda = \frac{1}{\varrho}\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} N\alpha(\epsilon) \tag{14}$$

where ϱ is the molar density and $n(\lambda)$ is the refractive index of the gas. The Verdet constant [7, 29–31], which arises in the Faraday effect, is given, in units of micro-minutes (orstead cm)$^{-1}$, by:

$$V(\epsilon) = r[1.00842 \times 10^6 \epsilon(dn/d\epsilon)] \tag{15}$$

The derivation of this result by Becquerel [32] applies to atoms and corresponds to $r = 1$; for molecules the coefficient r varies between 1 and 0.5 [29]. The derivative of the refractive index with respect to ϵ in Eq. (15) can be evaluated in terms of the DOSD through use of Eq. (14) and $(n^2-1)/(n^2+2) \approx (2/3)(n-1)$;

$$\epsilon(dn/d\epsilon) = 4\pi N\varrho E_H^2 a_0^3 \epsilon^2 \int_{E_0}^{\infty} dE(df/dE)(E^2 - \epsilon^2)^{-2} \tag{16}$$

In order to evaluate the various molecular dipole properties discussed in this section, reliable isotropic and anisotropic DOSDs are required. While it is extremely difficult to construct DOSDs that are accurate point by point as a function of photon energy, it is feasible to do this in a more global sense if appropriate input data is available. The resulting DOSDs yield reliable results for a wide variety of dipole properties. The construction of (globally) reliable isotropic DOSDs has been discussed extensively in the literature [1–3, 6–13]; the analogous problem for the anisotropic components of the DOSD is the subject of the remainder of this paper (see also [15]).

3. Construction of anisotropic DOSDs

Due to an essentially universal lack of symmetry analyzed dipole oscillator strength data as a function of excitation energy, the methods developed for the construction of isotropic molecular DOSDs require modification with respect to the construction of the anisotropic components of the DOSD. This modification has been discussed previously [15] and it will be reviewed briefly here for the $\perp$- and $\|$-DOSDs associated with linear molecules in Σ ground states.

3.1. *Method of construction*

The input data consists of the recommended (adopted) isotropic DOSD for the molecule and several known values of certain $\perp$ and $\|$ dipole properties which serve as anisotropic constraints. The molecules H_2 and N_2 will be considered as explicit examples in what follows.

To construct the ζ-component ($\zeta = \perp$ or $\|$) of the DOSD the energy spectrum for the isotropic DOSD, starting from the ζ-absorption threshold E_ζ, is divided into n intervals. The (df^ζ/dE) is related to (df/dE) in each interval by

$$(df^\zeta/dE) = (1 + b_i^\zeta)(df/dE), \qquad E_i \leqslant E \leqslant E_{i+1}, \quad i = 1, 2, \ldots, n \tag{17}$$

and such that the complete ζ-DOSD satisfies the specified constraints through the choice of the b_j^ζ.

The constraints used are furnished by the Thomas–Reiche–Kuhn sum rule [23–25], $S_0^\zeta = Z$ where Z is the number of electrons in the molecule, and by known values of other S_k^ζ or related properties. The constraints are written as a sum of n terms, one for each b_j^ζ occurring in Eq. (17), and the parameters b_j^ζ are determined by constrained least squares methods discussed in detail previously [1, 15].

3.2. *Anisotropic* DOSDs *for* H_2 *and* N_2

The recommended isotropic DOSDs of Zeiss et al. [1] are used to help construct the $\perp$- and $\|$-DOSDs for the H_2 and N_2 molecules and the intervals $(i = 1, 2, \ldots, n)$ occurring in Eq. (17) are identical to those employed in constructing the original isotropic DOSDs. The electronic absorption thresholds are taken from Huber and Herzberg [33] and are $E_\perp = 12.292$ and 12.500 eV and $E_\| = 11.183$ and 12.926 eV, respectively, for H_2 and N_2.

In addition to $S_0^\perp = S_0^\| = Z$ ($=2$ and 14 for H_2 and N_2, respectively) the following constraints were employed in the construction of the $\perp$- and $\|$-DOSDs for H_2 and N_2, respectively:

$$S_2^\perp(H_2) = 4.077, \qquad S_2^\|(H_2) = 2.925 \tag{18a}$$

$$S_1^\perp(H_2) = 1.831, \qquad S_1^\|(H_2) = 1.442 \tag{18b}$$

$$S_{-1}^\perp(H_2) = 2.881, \qquad S_{-1}^\|(H_2) = 3.525 \tag{18c}$$

$$S_{-2}^\perp(H_2) = 4.752, \qquad S_{-2}^\|(H_2) = 6.794 \tag{18d}$$

and

$$S_2^{\perp}(N_2) = 1.232 \times 10^4, \qquad S_2^{\parallel}(N_2) = 1.226 \times 10^4 \tag{19a}$$

$$S_1^{\perp}(N_2) = 139.5, \qquad S_1^{\parallel}(N_2) = 135.0 \tag{19b}$$

$$S_{-1}^{\perp}(N_2) = 8.806, \qquad S_{-1}^{\parallel}(N_2) = 10.840 \tag{19c}$$

$$\alpha^{\perp}(N_2, \lambda = 6328\ \text{Å}) = 10.34 a_0^3, \qquad \alpha^{\parallel}(N_2, \lambda = 6328\ \text{Å}) = 15.02 a_0^3 \tag{19d}$$

The evaluation and/or selection of these constraints has been discussed recently in detail [15]. The most reliable literature values for the relevant anisotropic dipole properties of H_2 and N_2 have been used for this purpose, see refs. [16–18, 34–38] and [27, 34, 36, 39–41], respectively, and the least squares constraint procedure has, in some cases, been used in an iterative fashion to achieve a reliable self-consistent set of constraints that yield the recommended results [1] for the corresponding isotropic dipole properties through Eq. (5).

The final $\perp$- and $\parallel$-DOSDs for H_2 and N_2 were obtained by using the constrained least squares method discussed briefly above with Eqs. (18) and (19), respectively, as anisotropic constraints. The resulting DOSDs are represented by a set of data points, with interconnecting interpolating functions, as discussed in detail, for isotropic DOSDs, in the literature [1]. The $\perp$- and $\parallel$-DOSDs were used to evaluate the various anisotropic and isotropic dipole properties discussed in Sect. 2 for H_2 and N_2 and a detailed comparison of these results, with selected literature values, is given in the next section.

A convenient discrete representation of the $\perp$- and $\parallel$-DOSDs for H_2 and N_2 can be found in [15]. These were obtained through the use of pseudo-DOSD techniques [2, 42, 43] and consist of ten $\perp$- and $\parallel$-pseudo states for each molecule obtained by requiring agreement between the $S_k^{\perp}$ and $S_k^{\parallel}$, $k = -17(1)2$, obtained directly from the original $\perp$- and $\parallel$-DOSDs and those obtained from their pseudo-DOSD representations. The original point by point $[(df^{\zeta}/dE)$ vs. $E]$ representations of the anisotropic H_2 and N_2 DOSDs are also available [44].

4. Anisotropic dipole properties of H_2 and N_2

The recommended results for the various dipole properties of H_2 and N_2 are summarized in Tables 1–10 which also contain selected literature values for the properties that have been obtained using a variety of techniques. Included in the literature results for the isotropic properties are those obtained from the original adopted isotropic DOSDs for H_2 and N_2 of Zeiss et al. [1].

4.1. *Dipole sums, logarithmic sums and mean excitation energies*

4.1.1. Molecular hydrogen. The $S_k^{\perp}$ and $S_k^{\parallel}$, and the S_k, all for $2 \geqslant k \geqslant -8$, are tabulated in Tables 1 and 2, respectively, while the corresponding logarithmic sums and mean excitation energies, for $2 \geqslant k \geqslant -2$, are listed in Table 3.

The values obtained by Victor and Dalgarno [7] for $S_k^{\perp}$, $S_k^{\parallel}$, and S_k, $k < 0$, are in very good agreement (within 0.1 to 2%) with those obtained here. Their work was a very early example of the construction of anisotropic DOSDs by constraining anisotropic dipole oscillator strength data to satisfy sum rules. As noted by them, their effective DOSDs give an inadequate representation of the

Table 1. Comparison of the DOSD results for the anisotropic components S_k^ζ of the dipole sums S_k, defined by Eq. (1), for H_2 with selected literature values

k	ζ	This work	Victor and Dalgarno [7]	Langhoff et al. [19]	Meyer [37]	Ford and Browne [16]	Martin et al. [45]
2	$\perp$	4.077^{a}	1.93			4.025	2.851
	$\parallel$	2.925^{a}	0.82			4.011	1.639
1	$\perp$	1.831^{a}	1.674			1.768	1.835
	$\parallel$	1.442^{a}	1.214			1.379	1.330
0	$\perp$	2.000^{a}	2.000	2.000	2.005	2.004	2.002
	$\parallel$	2.000^{a}	2.000	2.000	2.002	1.989	1.994
$-1/2$	$\perp$	2.347					
	$\parallel$	2.612					
-1	$\perp$	2.881^{a}	2.913		2.876	2.825	2.841
	$\parallel$	3.525^{a}	3.580		3.573	3.445	3.478
$-3/2$	$\perp$	3.654					
	$\parallel$	4.859					
-2	$\perp$	4.752^{a}	4.774	4.743	4.732	4.569	4.613
	$\parallel$	6.794^{a}	6.803	6.831	6.827	6.352	6.478
-3	$\perp$	8.479	8.433				
	$\parallel$	1.366(1)	1.348(1)				
-4	$\perp$	1.590(1)	1.567(1)	1.676(1)	1.581(1)		1.486(1)
	$\parallel$	2.815(1)	2.755(1)	2.654(1)	2.798(1)		2.503(1)
-5	$\perp$	3.078(1)					
	$\parallel$	5.893(1)					
-6	$\perp$	6.097(1)		6.79(1)	6.049(1)		5.466(1)
	$\parallel$	1.248(2)		1.09(2)	1.248(2)		1.045(2)
-8	$\perp$	2.501(2)		2.91(2)	2.464(2)		
	$\parallel$	5.735(2)		4.68(2)	5.818(2)		

[a] Used as constraints in the construction of the $\perp$- and $\parallel$-DOSDs for H_2

Table 2. Comparison of the DOSD results for the isotropic dipole sums S_k, obtained through Eq. (5) and our recommended S_k^ζ of Table 1, for H_2 with selected literature values

k	This work	Victor and Dalgarno [7]	Langhoff et al. [19]	Zeiss et al. [1]	Meyer [37]	Ford and Browne [16]	Martin et al. [45]	Geertsen et al. [46]
2	3.693	1.56		3.771		4.020	2.447	2.510
1	1.701	1.521		1.676		1.638	1.666	1.664
0	2.000	2.000	2.000	2.000	2.004	1.999	1.999	2.000
$-1/2$	2.435			2.440				
-1	3.096	3.135		3.100	3.108	3.032	3.053	3.054
$-3/2$	4.056			4.057				
-2	5.433	5.450	5.439	5.428	5.430	5.163	5.234	5.228
-3	1.021(1)	1.012(1)		1.018(1)				9.551
-4	1.998(1)	1.963(1)	2.002(1)	1.996(1)	1.987(1)		1.825(1)	1.817(1)
-5	4.017(1)			4.027(1)				3.553(1)
-6	8.224(1)		8.16(1)	8.294(1)	8.193(1)		7.129(1)	7.077(1)
-8	3.579(2)		3.50(2)	3.670(2)	3.582(1)			

Table 3. Comparison of the DOSD results for the anisotropic components L_k^ζ and I_k^ζ of the logarithmic dipole sums L_k and average energies I_k, and their isotropic averages defined by Eqs. (5) and (11) respectively, for H_2 with selected literature values. The I_k are given in units of eV. Victor and Dalgarno [7] obtained $I_0 = 18.6$ eV

	Anisotropic (this work)		Isotropic			
Property	$\zeta = \perp$	$\zeta = \parallel$	This work	Zeiss et al. [1]	Ford and Browne [16]^a	Geertsen et al. [46]^a
L_2	8.420	6.832	7.891	8.825		
L_1	2.896(−1)	−1.144(−1)	1.549(−1)	1.141(−1)		
L_0	−5.279(−1)	−9.783(−1)	−6.780(−1)	−6.908(−1)		
L_{-1}	−1.285	−2.198	−1.589	−1.586		
L_{-2}	−2.595	−4.632	−3.274	−3.260		
I_2	2.146(2)	2.813(2)	2.305(2)	2.825(2)	4.466(1)	1.297(1)
I_1	3.187(1)	2.514(1)	2.981(1)	2.913(1)	2.539(1)	2.931(1)
I_0	2.090(1)	1.668(1)	1.939(1)	1.926(1)	1.921(1)	1.912(1)
I_{-1}	1.742(1)	1.459(1)	1.629(1)	1.631(1)	1.643(1)	1.635(1)
I_{-2}	1.576(1)	1.376(1)	1.490(1)	1.493(1)		1.503(1)

[a] Their mean excitation energies include the effects of vibrational and rotational averaging

higher energy portion of the absorption spectrum and therefore yields poor results for dipole sums like S_1 and S_2 which are dominated by this part of the DOSD.

Also given in Tables 1 and 2 are results for $k = -8(2)0$, due to Langhoff et al. [19], based on Padé approximate and related bounding techniques. For $k = -2$ their results are in excellent agreement (within 0.5%) with those of this paper. However, for the other values of $k < 0$ their $S_k^\perp$ values are 5 to 14% too high, while their $S_k^\parallel$ are 6 to 23% too low and hence their predicted anisotropies in these dipole sums are much smaller than our recommended values for the $(S_k^\parallel - S_k^\perp)$. The discrepancies between the two sets of results generally increases with decreasing k and the estimated errors [19] in the Padé calculations are $\pm(5-10)\%$ for $k = -2$ and -4 and $\pm 15\%$ for $k = -6$ and -8. It is interesting to note that, because of a cancellation of errors, the anisotropic S_k^ζ of Langhoff et al. [19] yields results, through Eq. (5), for the isotropic S_k that agree well (to within 2%) with our values for $k = -4, -6, -8$.

The agreement (Table 2) between the recommended isotropic dipole sums S_k of this paper and those of Zeiss et al. [1] is excellent for all k and well within the estimated errors in the original isotropic calculations.

Use has already been made of the precise *ab initio* results for the S_{-2}^ζ, due to Bishop and Cheung [17] and Rychlewski [18], as constraints (see 18(d)) in the construction of the anisotropic DOSDs for H_2. Other *ab initio* results for the S_k^ζ and S_k are listed in Tables 1 and 2.

The most extensive set of *ab initio* results for $k \leqslant 0$ is due to Meyer [37] and his values for the S_k^ζ and the S_k agree with our recommended results to within 1.5% and .6%, respectively, for common values of k. The *ab initio* results for $S_{-1}^\perp$ and $S_{-1}^\parallel$ due to Wolniewicz [38] are ~.1% and ~.8% lower than those of Meyer [37]. Meyer's values include the effects of rotational and vibrational averaging, whereas all the other *ab initio* results listed in Tables 1–3, except for the mean excitation energies I_k, are for the internuclear distance held fixed at the equilibrium value. As discussed by Ford and Browne [16], these effects can be significant and, for example, can increase S_{-2} by ~4% and decrease I_0 by ~1.6%. Their vibrationally and rotationally averaged results for $k = -2$ are $S^{\perp}_{-2} = 4.738$, $S^{\parallel}_{-2} = 6.743$ and $S_{-2} = 5.406$.

Ab initio results for the S_k^{ζ} and S_k, for $k > 0$ as well as $k < 0$, have been obtained by Ford and Browne [16] and by Martin et al. [45]. For $k < 0$ these results are generally inferior to those of Meyer [37] and some of the discrepancies are due to the neglect of vibrational and rotational averaging effects in [16, 45]. For $k > 0$ the *ab initio* results are of variable quality. For example, the random phase approximation values of Martin et al. [45] agree with our values to within 0.2% and −8% for $S_1^{\perp}$ and $S_1^{\parallel}$, respectively; their results for the S_2^{ζ} are much too low. On the other hand, Ford and Browne's [16] value for $S_2^{\perp}$ agrees with our recommended result to within −1.3% whereas their result for $S_2^{\parallel}$ is ~27% too high; the analogous values for the S_1^{ζ} are lower than our results by ~4%. The *ab initio* results of Geertsen et al. [46], evaluated using the polarization propagator method and available only for the isotropic sums S_k for $k = -6(1)2$, are between 1.4 to 47% lower than our values with the best agreement occurring for $k = 1(-2\%)$ and $k = -1(-1.4\%)$; their $S_0 = Z$.

Apparently there are no literature values available for the ⊥- and ∥-components of the logarithmic dipole sums L_k and the mean excitation energies I_k. The isotropic mean excitation energy for stopping, I_0, obtained here agrees well with the isotropic DOSD result of Zeiss et al. [1] and with the *ab initio* calculations of Ford and Browne [16], and Geertsen et al. [46], and all these results agree well with the value of 19.2 eV obtained by Gerhart [47] through the use of semiempirical DOSD methods; the result of Victor and Dalgarno [7] is ~4% too low. It should be noted that the *ab initio* values of all the mean excitation energies in Table 3 *do* include the effects of vibrational and rotational averaging.

For $k < 0$ all the I_k results given in Table 3 agree to within 1% with each other. The agreement for the straggling mean excitation energy I_1 is to within 2% except for the value obtained by Ford and Browne [16] which is ~17% too low. For I_2 there is substantial disagreement between the values listed. The *ab initio* results due to Ford and Browne [16] and Geertsen et al. [46] disagree by ~48% and −78%, respectively, with respect to our result which itself is ~18% lower than the isotropic DOSD value obtained by Zeiss et al. [1].

It is interesting to note that while our results for the S_k agree well with those of Zeiss et al. [1], those for some of the L_k and for I_2 do not. The reason for this is associated with the different photon energy dependencies of the L_k relative to the S_k and because the L_k have negative contributions, for $E < 27.2$ eV arising from the factor $\ln(E/E_H)$ occurring in (2); the contributions to the S_k, for all E, are of course positive. These features of the logarithmic dipole sums, relative to the S_k, have been discussed in detail by Kumar and Meath [12].

For $k = 2$ the dipole properties are dominated by the high energy portion of the DOSD, more so for L_2 than for S_2; the contributions from $E \geqslant 100$ eV to L_2 and S_2 are ~95% and ~56%, respectively, with the negative contribution to L_2 being only ~3% of the positive contribution. Thus L_2 is much more sensitive than S_2 to the constraints placed on the high energy portion of the DOSD. In the construction of the isotropic DOSD of Zeiss et al. [1] only the constraint $S_0 = Z$ was used for this purpose; this has been augmented in our work by also using known values of S_1 and S_2 as constraints ([15], see Sect. 3). The effects of the different constraints is ~2% for S_2 and ~10% for L_2.

The situation is considerably different for $k = 1$. Here the negative contribution to L_1 is $\sim 75\%$ of the positive one leading to a very small positive value of L_1. Hence the effects of the differences between the isotropic DOSD of this paper and that of Zeiss et al. become magnified (to 35%) in the property L_1. For $k = 0$, the magnitude of the negative contributions to L_0 is ~ 4.7 times the positive contribution. This leads to a negative small value of L_0 which is dominated by the low energy part of the DOSD which is not strongly effected by the values of S_1 and S_2 used to help constrain the DOSDs constructed here. The disagreement between our L_0 value and that of Zeiss et al. [1] is only $\sim 2\%$. As k decreases to -1 and -2 the L_k values increase, in a negative sense, and the discrepancies between the two sets of isotropic DOSD values become small ($\leqslant .4\%$).

The results for the mean excitation energies in Eq. (11) depend on the factor $\exp[L_k/S_k]$ and therefore depend on the ratio of the two different types of dipole sums. The exponential function is not a sensitive function of the ratio if (L_k/S_k) is small which is the case for $k = 1$. For $k = 2$, $L_2/S_2 = 2.137$ and 2.340, respectively, for our results versus those of Zeiss et al. [1], leading to a discrepancy of $\sim 18\%$ in the corresponding values of I_2. For $k = 1$, $L_1/S_1 = .0911$ and 0.0681, respectively, leading to a difference of only 2% (whereas the discrepancy in L_1 was $\sim 35\%$).

The recommended values of the isotropic dipole sums obtained in this paper are to be preferred to those of Zeiss et al. [1] for the dipole properties ($k = 2, 1$) dominated by the higher energy portions of the DOSDs.

4.1.2. Molecular nitrogen. Generally speaking, far fewer high-quality calculations of the dipole properties of N_2 are available relative to H_2. Our results for the S^{ζ}_k and the S_k are listed in Table 4, those for the L^{ζ}_k, I^{ζ}_k, L_k and I_k in Table 5.

The Padé approximate results of Langhoff et al. [19], for the S^{ζ}_k and the S_k, agree with our results to within 5% and 3%, respectively, for $k = -8(2)-2$ with the agreement improving with increasing k and the results for the $S^{\parallel}_k$ being slightly more reliable than those for the $S^{\perp}_k$; the discrepancies between the two sets of results are far less than the estimated errors [19] (± 5–10% for S_{-2} and S_{-4}, $\pm 15\%$ for S_{-6} and S_{-8}) in the Padé calculations.

The *ab initio* calculations for the S^{ζ}_{-2} and S_{-2} due to Maroulis and Thakkar [40] and Langhoff et al. [41], namely $S^{\perp}_{-2} = 10.13$ and 10.19, $S^{\parallel}_{-2} = 14.77$ and 14.76 and $S_{-2} = 11.68$ and 11.71, respectively, are in excellent agreement with our results. Indeed these *ab initio* results were used to help assess the reliability of the constraint of Eq. (19d) as discussed in some detail in Meath and Kumar [15]. The *ab initio* results do not include the effects of vibrational and rotational averaging. These effects have been estimated by Maroulis and Thakkar [40], using the polarizability derivatives of Langhoff et al. [41], and are relatively small ($+\sim 0.02$ and ~ 0.07 for $S^{\perp}_{-2}$ and $S^{\parallel}_{-2}$, respectively).

The multiple scattering technique has been used by Kosman and Wallace [39] to construct a representation of the entire oscillator strength distribution of N_2 (without including the effects of vibrational and rotational averaging). The corresponding results [39] for the S^{ζ}_k, $k = -2(1)2$, and the S_k, $k = -6(1)2$, are in excellent agreement with our recommended values for $k = 1, 0$. For all other values of k, as recognized by Kosman and Wallace [39], the multiple scattering results are much too high.

There are relatively few literature results for the logarithmic dipole sums and the mean excitation energies listed in Table 5, especially for their anisotropic components. The isotropic results obtained by Kosman and Wallace [39] are in

Table 4. Comparison of the DOSD results for the anisotropic components S_k^ζ of the dipole sums S_k, and their isotropic averages defined by Eq. (5), for N_2 with selected literature values

	Perpendicular			Parallel			Isotropic			
k	This work	Langhoff et al. [19]	Kosman and Wallace [39]	This work	Langhoff et al. [19]	Kosman and Wallace [39]	This work	Zeiss et al. [1]	Langhoff et al. [19]	Kosman and Wallace [39]
2	1.232(4)[a]		1.523(4)	1.226(4)[a]		1.519(4)	1.230(4)	1.230(4)		1.521(4)
1	1.395(2)[a]		1.404(2)	1.350(2)[a]		1.356(2)	1.380(2)	1.380(2)		1.388(2)
0	1.400(1)[a]	1.400(1)	1.398(1)	1.400(1)[a]	1.400(1)	1.398(1)	1.400(1)	1.400(1)	1.400(1)	1.398(1)
−1/2	9.702			1.073(1)			1.004(1)	1.005(1)		
−1	8.806[a]		1.001(1)	1.084(1)[a]		1.475(1)	9.484	9.484		1.159(1)
−3/2	9.122			1.230(1)			1.018(1)	1.018(1)		
−2	1.021(1)	1.020(1)	1.450(1)	1.480(1)	1.482(1)	3.162(1)	1.174(1)	1.174(1)	1.174(1)	2.021(1)
−3	1.480(1)			2.365(1)			1.775(1)	1.781(1)		4.472(1)
−4	2.423(1)	2.466(1)		4.084(1)	4.118(1)		2.977(1)	3.011(1)	3.017(1)	1.106(2)
−5	4.270(1)			7.383(1)			5.308(1)	5.428(1)		2.890(2)
−6	7.874(1)	8.07(1)		1.374(2)	1.36(2)		9.831(1)	1.018(2)	9.913(1)	7.778(2)
−8	2.903(2)	3.06(2)		5.028(2)	5.09(2)		3.611(2)	3.846(2)	3.737(2)	

[a] Used as constraints in the construction of the ⊥- and ∥-DOSD for N_2

Table 5. Comparison of the DOSD results for the anisotropic components L_k^ζ and I_k^ζ of the logarithmic dipole sums L_k and average energies I_k, and their isotropic averages defined by Eqs. (5) and (11), respectively, for N_2 with selected literature values. The I_k are given in units of eV

Property	Anisotropic (this work)		Isotropic		
	$\zeta = \perp$	$\zeta = \parallel$	This work	Zeiss et al. [1]	Kosman and Wallace [39]
L_2	7.661(4)	7.645(4)	7.655(4)	7.682(4)	1.210(5)
L_1	4.707(2)	4.603(2)	4.672(2)	4.675(2)	4.688(2)
L_0	1.618(1)	1.394(1)	1.543(1)	1.541(1)	1.459(1)
L_{-1}	3.015(−1)	−1.806	−4.008(−1)	−3.915(−1)	−3.995
L_{-2}	−2.900	−6.091	−3.964	−3.980	−1.431(1)
I_2	1.365(4)	1.389(4)	1.374(4)	1.402(4)	7.757(4)
I_1	7.945(2)	8.231(2)	8.036(2)	8.047(2)	7.979(2)
I_0	8.642(1)	7.364(1)	8.192(1)	8.184(1)	7.736(1)
I_{-1}	2.816(1)	2.304(1)	2.609(1)	2.611(1)	1.928(1)
I_{-2}	2.048(1)	1.803(1)	1.941(1)	1.939(1)	1.340(1)

good agreement with our values only for $k = 1, 0$. For example, the multiple scattering results for I_1, I_0 and I_{-1} are ~0.7%, ~6% and ~35% lower, respectively, than the recommended values. The results for the L_k and I_k obtained from the recommended isotropic DOSD for N_2 of Zeiss et al. [1] agree very well with our values and the stopping power average energy $I_0 = 81.9$ eV is in agreement with the value adopted by the International Commission on Radiation Units and Measurements [48].

Aside from S_{-8}, where the disagreement is ~6%, all our isotropic dipole properties of N_2 agree very well with those evaluated from the adopted DOSD for N_2 of Zeiss et al. [1].

4.2. Dynamic dipole polarizabilities and their anisotropics

4.2.1. Molecular hydrogen. Our results for the dynamic dipole polarizability $\alpha(\epsilon)$, and its anisotropy $\gamma(\epsilon)$, for H_2, as a function of wavelength ($\lambda = \infty$, $6328.0\ \text{Å} \geqslant \lambda \geqslant 1215.7\ \text{Å}$), are compared in Table 6 with selected literature values. All the *ab initio* calculations quoted have taken vibrational and rotational averaging effects into account.

For $\alpha(\epsilon)$ there is excellent agreement, for all common wavelengths, between our results and the constrained DOS values of Victor and Dalgarno [7], the very accurate *ab initio* calculations of Bishop and Cheung [17], and the experimental results of Koch [49] and Kirn [50], with errors of ⩽.2% [51], and Gill and Heddle [52] (experimental error 2%). The maximum discrepancies between our values and those of the other authors are, respectively, ⩽.3%, ⩽.08% except at $\lambda = 1215.7$ Å where it is .5%, and ⩽.3% except at $\lambda = 1215.7$ Å where the disagreement with Gill and Heddle is .5%. The *ab initio* calculations of Meyer [37] and Rychlewski [18], carried out for fewer wavelengths and not included in Table 6, are in excellent agreement with the results listed in Table 6 except at $\lambda = 1215.7$ Å where Rychlewski's result is 1.5% higher than our value; at

Table 6. Comparison of the DOSD results for the dynamic polarizability $\alpha(\epsilon)$ of H_2, and its anisotropy $\gamma(\epsilon)$, with selected literature values, as a function of wavelength λ

	Dynamic polarizability $\alpha(\epsilon)$				Anisotropy $\gamma(\epsilon)$			
λ/Å	This work	Victor and Dalgarno [7]	Bishop and Cheung [17]	Experiment[a]	This work	Victor and Dalgarno [7]	Bishop and Cheung [17]	Rychlewski [18]
∞	5.433	5.450	5.434		2.042	2.029	2.037	2.042
6328.0	5.539	5.554	5.539		2.107	2.092	2.101	2.102
5462.3	5.576	5.591	5.577	5.582	2.130	2.115	2.123	2.129
4359.6	5.661	5.675	5.662	5.667	2.184	2.168	2.175	2.182
4079.0	5.696	5.708	5.696	5.701	2.206	2.188	2.196	2.203
4047.7	5.700	5.713	5.700	5.705	2.208	2.191	2.199	2.206
3342.4	5.835	5.845	5.835	5.840	2.294	2.274	2.283	2.290
2968.1	5.954	5.963	5.954	5.960	2.371	2.350	2.358	2.365
2753.6	6.050	6.056	6.049	6.055	2.433	2.410	2.419	2.428
2535.6	6.178	6.182	6.177	6.183	2.517	2.492	2.501	
2379.1	6.297	6.299	6.296	6.303	2.597	2.569	2.580	2.592
2302.9	6.367	6.368	6.366	6.384	2.644	2.615	2.626	2.639
1990.5	6.773	6.766	6.771	6.771	2.923	2.889	2.902	
1935.8	6.873	6.865	6.871	6.868	2.993	2.958	2.972	2.989
1862.7	7.028	7.017	7.026	7.017	3.103	3.067	3.081	
1854.6	7.047	7.035	7.045	7.035	3.117	3.080	3.095	
1700.0	7.489	7.471	7.487		3.440	3.401	3.419	
1600.0	7.896	7.872	7.895		3.748	3.710	3.730	
1500.0	8.462	8.431	8.463		4.194	4.159	4.185	
1400.0	9.298	9.262	9.305		4.889	4.871	4.906	
1215.7	1.273(1)	1.277(1)	1.280(1)	1.28(1)	8.224	8.495	8.537	8.808

[a] Koch [49] and Kirn [50] for 5462 Å $\geqslant \lambda \geqslant$ 1854 Å and Gill and Heddle [52] for λ = 1215.7 Å

$\lambda = 1215.7$ Å, Meyer's value agrees with our result to within .07%. Aside from this value of λ, Rychlewski's [18] and Bishop and Cheung's [17] values are almost in precise agreement for common wavelengths. The earlier *ab initio* results of Ford and Browne [16] are consistently lower than the values of $\alpha(\epsilon)$ given in Table 6 by between .5% and 1.5%.

MacAdam and Ramsey [53] have measured the polarizability anisotropy at zero frequency by using beam-magnetic resonance methods to obtain $\gamma(\lambda = \infty) = 2.035 \pm 0.003$. Our result, and those of Victor and Dalgarno [7] and Bishop and Cheung [17], agree well with the experimental result (see Table 6) but only the latter agrees within the quoted (small) experimental uncertainty. The *ab initio* calculation of Rychlewski [18] agrees precisely with our DOSD value.

Bearing in mind that the anisotropy of the dipole polarizability is generally more difficult to calculate accurately than $\alpha(\epsilon)$, the agreement between the *ab initio* calculations of Bishop and Cheung [17] and our results is remarkable, within .7% for all wavelengths quoted in Table 6 except for $\lambda = 1218.7$ Å where our result is 3.7% lower than the *ab initio* value. The agreement with Victor and Dalgarno [7] is also very good, being to within 1.2% except at $\lambda = 1215.7$ Å where it is 3%. Our values of $\gamma(\epsilon)$ are also in excellent agreement ($\leqslant$.3% except at $\lambda = 1215.7$ Å where it is 6.5%) with the more limited *ab initio* calculations of Rychlewski [18], which are included in Table 6 for $\gamma(\epsilon)$. Indeed, aside from $\lambda = 1215.7$ Å, Rychlewski's results are in closer agreement with our values than are those of Bishop and Cheung [17]. The *ab initio* results of Ford and Browne [16] disagree with the values reported in Table 6 by ~2–3% as a function of wavelength.

Another type of dipole polarizability anisotropy, $\kappa(\epsilon) = \gamma(\epsilon)/(3\alpha(\epsilon))$, has been measured for H_2 at the single wavelength $\lambda = 6328$ Å by Bridge and Buckingham [27]. Our result of 0.127 is in excellent agreement with the experimental value $\kappa(\lambda = 6328\text{ Å}) = 0.128 \pm .002$; the values of κ corresponding to the other relevant data [7, 17, 18] in Table 6 are 0.126, 0.126 and 0.127, respectively.

4.2.2. Molecular nitrogen. The DOSD results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$ are compared with literature values in Table 7 over the wavelength domain $\lambda = \infty$, $9787.2\text{ Å} \geqslant \lambda \geqslant 1139.0\text{ Å}$. Our calculations provide the only data for a significant number of wavelengths in this region.

The results of this paper for the dynamic polarizability of N_2 are in excellent agreement (to within .1%) with the experimental data of Peck and Khanna [54] (errors $\leqslant$.03%) for all common wavelengths. The Padé approximant based values of Langhoff [55] agree, within their quoted errors, with our results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$. The *ab initio* second order polarization propagator approximation results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$, due to Stroyer-Hansen and Svendson [56], are consistently lower than our DOSD values by ~1.5% and ~11%, respectively, for common wavelengths. The SOPPA results are for a fixed internuclear separation but it seems unlikely that the effects of vibrational and rotational averaging could account for the discrepancies with the other results in Table 7 (see Sect. 4.1.2.). The value for the anisotropy parameter $\kappa(\epsilon)$ for $\lambda = 6328.0$ Å calculated from our results, $\kappa = 0.131$, agrees precisely with the experimental results of Bridge and Buckingham [27] since their result for the corresponding depolarization ratio ϱ_v^T was used as a constraint for the construction of the N_2-DOSDs.

Table 7. Comparison of the DOSD results for $\alpha(\epsilon)$ of N_2, and its anisotropy $\gamma(\epsilon)$, with selected literature values, as a function of wavelength λ

	Dynamic polarizability $\alpha(\epsilon)$				Anisotropy $\gamma(\epsilon)$		
λ/Å	This work	Langhoff [55]	Stroyer-Hansen and Svendsen [56]	Peck and Khanna [54]	This work	Langhoff [55]	Stroyer-Hansen and Svendsen [56]
∞	1.174(1)	1.173(1)	1.157(1)		4.593	4.6	
9787.2	1.180(1)			1.181(1)	4.629		
9660.4	1.181(1)			1.181(1)	4.630		
9227.0	1.181(1)			1.182(1)	4.634		
9125.5	1.181(1)			1.182(1)	4.635		
9112.0	1.181(1)	1.183(1)			4.635	4.6	
8226.8	1.183(1)			1.183(1)	4.644		
7247.2	1.186(1)			1.186(1)	4.660		
6328.0	1.190(1)		1.172(1)		4.681		4.23
5462.3	1.195(1)			1.196(1)	4.711		
5145.0	1.198(1)		1.181(1)		4.727		4.27
5087.2	1.198(1)			1.199(1)	4.730		
4880.0	1.201(1)		1.183(1)		4.742		4.28
4801.3	1.202(1)			1.202(1)	4.747		
4679.5	1.203(1)			1.204(1)	4.756		
4556.0	1.205(1)	1.207(1)			4.765	4.7	
4358.0	1.208(1)		1.190(1)		4.782		4.32
3638.0	1.223(1)		1.206(1)		4.869		4.39
3511.0	1.227(1)		1.210(1)		4.890		4.41
3037.3	1.246(1)	1.247(1)			4.999	5.0	
3000.0	1.248(1)		1.231(1)		5.010		4.51
2778.0	1.312(1)	1.310(1)			5.367	5.4	
2000.0	1.361(1)		1.342(1)		5.650		5.04
1822.4	1.410(1)	1.417(1)			5.928	5.9	
1518.7	1.562(1)	1.563(1)			6.796	6.7	
1301.7	1.816(1)	1.823(1) ± 2.4(−1)			8.223	8.2 ± 0.1	
1139.0	2.319(1)	2.343(1) ± 1.34			1.087(1)	1.20(1) ± 1.0	

4.3. Total depolarization ratios

In Table 8, we list our results for the total depolarization ratio ϱ_v^T, as a function of wavelength for 6328.0 Å $\geqslant \lambda \geqslant$ 1215.7 Å, for H_2 and N_2. Available literature experimental values are included in the table for N_2.

4.3.1. Molecular hydrogen. For H_2 our result at $\lambda = 6328.0$ Å agrees well with that of Bridge and Buckingham [27], $100\,\varrho_v^T = 0.9703 \pm .03$, obtained by using Eq. (6) and their value of $\kappa = \gamma/(3\alpha)$ at this wavelength. The measurement of Rowell et al. [57] at 4880 Å, $100\,\varrho_v^T = 0.954 \pm .003$, is ~1.5% lower than our DOSD value. As our results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$ are in excellent agreement with the very reliable *ab initio* calculations of Bishop and Cheung [17], and Rychlewski [18], see Sect. 4.2.1, the error assigned to the experimental measurement is probably too small. Ford and Browne [16] have also discussed the depolarization ratios for H_2 in some detail and the results for $100\,\varrho_v^T = 0.926$ and 0.940, obtained from their calculated $\alpha(\epsilon)$ and $\gamma(\epsilon)$ at $\lambda = 6328.0$ Å and 4880 Å, respectively, are considerably too low.

4.3.2. Molecular nitrogen. For N_2, a number of experimental measurements are available. We reproduce the accurate (error .5%) results of Bridge and Buckingham [27] at $\lambda = 6328.0$ Å since it was used to establish the constraints of Eq. (19d) employed in the construction of the anisotropic DOSDs for N_2 through the use of a very reliable value of $\alpha(\lambda = 6328.0$ Å). The more recent measurements of Baas and Van den Hout [58] at $\lambda = 6328.0$ Å and 5145 Å agree, with their quoted error of 3%, with Bridge and Buckingham and our results. Our values, for $\lambda = 5148$ Å, 4880 Å and 4579 Å, are ~3.5% to 5% lower than the results of Alms et al. [21] whose quoted experimental errors are ~2–3%. A rough extrapolation of their results to $\lambda = 6328$ Å suggests a value of ϱ_v^T considerably

Table 8. Comparison of the DOSD results for the total depolarization ratio ϱ_v^T for H_2 and N_2, as a function of wavelength, with experimental literature values (for the H_2 literature values, see main text). The results are quoted as $100\varrho_v^T$ in the table

	H_2	N_2			
λ/Å	This work	This work	Alms et al. [21]	Baas and Van den Hout [58]	Rowell et al. [57]
6328.0	9.528(−1)	1.018		1.00 ± 0.03	
5462.3	9.608(−1)	1.022			
5148.0	9.648(−1)	1.024	1.06 ± 0.02		
5145.0	9.649(−1)	1.024		1.01 ± 0.03	
4880.0	9.689(−1)	1.026	1.07 ± 0.02		1.08 ± 0.01
4579.0	9.744(−1)	1.028	1.08 ± 0.03		
4359.6	9.792(−1)	1.031			
4047.7	9.875(−1)	1.035			
3342.4	1.017	1.048			
2302.9	1.132	1.098			
1990.5	1.221	1.132			
1862.7	1.278	1.153			
1600.0	1.473	1.214			
1400.0	1.799	1.290			
1215.7	2.684	1.397			

Table 9. Comparison of the DOSD results for the Rayleigh scattering cross sections $Q_{\mathrm{Ray}}(\epsilon)$ for H_2 and N_2, as a function of wavelength, with literature results. The results are given in units of 10^{-27} cm^2

	Molecular hydrogen					Molecular nitrogen	
λ/Å	This work	Victor and Dalgarno [7]	Langhoff [55]	Martin et al. [45]	λ/Å	This work	Dalgarno et al. [28]
6328.0	5.661(−1)	5.69(−1)		5.23(−1)	9000.0	6.310(−1)	6.10(−1)
5462.3	1.034	1.04	1.04 ± 0.00	9.53(−1)	8000.0	1.014	9.80(−1)
4359.6	2.628	2.64	2.64 ± 0.01	2.42	7000.0	1.740	1.69
4079.0	3.472	3.48	3.48 ± 0.01	3.19	6328.0	2.618	
4047.7	3.586	3.60			6000.0	3.249	3.14
3342.4	8.090	8.11	8.09 ± 0.02	7.42	5500.0	4.628	4.47
2968.1	1.356(1)	1.36(1)	1.353(1) ± 0.04	1.24(1)	5462.3	4.759	
2753.6	1.891(1)	1.89(1)	1.882(1) ± 0.05	1.73(1)	5148.0	6.060	
2535.6	2.745(1)	2.75(1)	2.724(1) ± 0.07		5000.0	6.828	6.60
2379.1	3.683(1)	3.68(1)		3.35(1)	4880.0	7.541	
2302.9	4.291(1)	4.29(1)	4.241(1) ± 0.12	3.89(1)	4500.0	1.052(1)	1.02(1)
1990.5	8.725(1)	8.70(1)			4000.0	1.709(1)	1.65(1)
1935.8	1.005(2)	1.00(2)	9.821(1) ± 0.30	9.02(1)	3000.0	5.714(1)	5.52(1)
1862.7	1.227(2)	1.220(2)			2000.0	3.448(2)	3.34(2)
1854.6	1.256(2)	1.250(2)	1.222(2) ± 0.4	1.12(2)	1700.0	7.582(2)	7.36(2)
1700.0	2.016(2)	2.000(2)		1.78(2)	1600.0	1.036(3)	1.00(3)
1600.0	2.864(2)	2.840(2)		2.51(2)	1500.0	1.468(3)	1.43(3)
1500.0	4.277(2)	4.240(2)		3.70(2)	1400.0	2.181(3)	2.08(3)
1400.0	6.849(2)	6.800(2)		5.81(2)	1300.0	3.472(3)	3.43(3)
1300.0	1.224(3)	1.220(2)		1.00(3)	1215.7	5.577(3)	5.62(3)
1215.7	2.323(3)	2.350(3)		1.79(3)			

higher than the accurate result of Bridge and Buckingham. More recent measurements [59], involving the same group and molecules in common with [21], indicate that the results of Alms et al. [21] are probably too high by ~2–3%. The value of ϱ_v^T, at $\lambda = 4880$ Å, due to Rowell et al. [57] is higher than that of Alms et al. [21].

4.4. Rayleigh scattering cross sections

The Rayleigh scattering cross sections $Q_{\mathrm{Ray}}(\epsilon)$ obtained by using Eq. (8) and our results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$ are given in Table 9, as a function of wavelength, for H_2 and N_2. Included in the table are calculated literature results; apparently no experimental values are available. $Q_{\mathrm{Ray}}(\epsilon)$ is of interest, for example, in astrophysical applications [16, 60, 61].

4.4.1. Molecular hydrogen. For H_2 our results agree with Victor and Dalgarno [7], to well within 1%, over the whole range of wavelengths considered. The cross sections due to Langhoff [55] are in essential agreement with these values for $\lambda \geqslant 2753.6$ Å but as λ decreases the discrepancies become significant. The random phase approximation calculations of Martin et al. [45] are much too low for all the relevant wavelengths. A significant part of the discrepancy between their values, and the other results, arises because their calculations are carried out at a fixed value of the internuclear distance. The neglect of vibrational and rotational averaging leads to results for $\alpha(\epsilon)$ that are too low (by ~4% for $\alpha(\epsilon = 0)$, see Sect. 4.1.1). The impact of these effects is magnified in Q_{Ray} due to the $(\alpha(\epsilon))^2$ dependence of the dominant term in Eq. (8).

Ford and Browne [16] have computed Q_{Ray} for H_2 at the Lyman α wavelength (1215.7 Å). They used an expression for Q_{Ray} that includes rotational fine structure [62] and obtained $2.265 \times 10^{-24}\,\mathrm{cm}^2$; using their results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$, at the appropriate wavelength, in the corresponding averaged result of Eq. (8), we obtain $2.292 \times 10^{-24}\,\mathrm{cm}^2$. The later result is ~1.3% lower than our value of Q_{Ray} at the Lyman α wavelength.

4.4.2. Molecular nitrogen. The results for Q_{Ray} for N_2, due to Dalgarno et al. [28], were calculated assuming the contribution of $\gamma(\epsilon)$ in Eq. (8) is small relative to that of $\alpha(\epsilon)$; values of $\gamma(\epsilon)$ were not available to these authors. A model isotropic dipole oscillator strength spectrum was construced in [28], through the use of then available DOS values, refractive indices, and sum rules for N_2, and used to evaluate $\alpha(\epsilon)$ and hence Q_{Ray}. Using our results for $\alpha(\epsilon)$ and $\gamma(\epsilon)$ we find that the contribution to Q_{Ray} due to the second term in Eq. (8) is ~3.3–3.4% for $9000\,\text{Å} \geqslant \lambda \geqslant 3000\,\text{Å}$, increasing to 3.7%, 3.8%, 4%, and 7.4% at $\lambda = 2000$, 2822, 1519 and 1302 Å, respectively. Thus the discrepancies between the values of Dalgarno et al. [28] and our results for Q_{Ray} for $9000\,\text{Å} \geqslant \lambda \geqslant 2000\,\text{Å}$ seem to be due to their neglect of the second term in Eq. (8) while for smaller λ they are also due to unreliable results for $\alpha(\epsilon)$ as well. As pointed out by Dalgarno et al., their results for the refractive index of N_2, and hence $\alpha(\epsilon)$, become less reliable for $\lambda < 2000$ Å.

4.5. *Verdet constants for* H_2 *and* N_2

Table 10 compares our calculated parameter $r = V(\epsilon)/V_N(\epsilon)$, where V_N is given by Eq. (15) with $r = 1$, for H_2 and N_2 with literature results. The $V(\epsilon)$ are taken to be the experimental measurements of Ingersoll and Liebenberg [30].

For H_2 our results agree with the recent *ab initio* calculations of Bishop and Cybulski [63] to within $\leqslant .4\%$ for all wavelengths considered in Table 10. The results of Langhoff [55] are in excellent agreement with these results. On the other hand, the random phase approximation calculations of Martin et al. [45], which do not take account of vibrational and rotational averaging effects, are ~9% higher for all λ. Apparently much of this discrepancy is due to the neglect of these effects which, according to Bishop and Cybulski [63], increase V_N by ~10%. It is also relevant to point out that these authors [63] have evaluated $V(\epsilon)$ directly, without recourse to the Becquerel equation, and have obtained results that agree with experiment to within the (probable [63]) experimental error of $\leqslant 1\%$.

For N_2, the results of Langhoff [55] for r are from one to two percent lower than our values for all values of λ listed in Table 10.

It is interesting to compare the results of Table 10 with those of Darwin and Watson [31] based on the dispersion relation for the refractive index of H_2 and N_2 given by Cuthbertson and Cuthbertson [64] and older Verdet constant measurements [65]. They concluded that $r = 1$ and $r = .63$ for H_2 and N_2 respectively; the latter result is in excellent agreement with those of Langhoff and

Table 10. Comparison of the DOSD results for the parameter $r = V(\epsilon)/V_N(\epsilon)$, where V_N is defined by Eq. (15) with $r = 1$ and the $V(\epsilon)$ are the experimental measurements of the Verdet constants due to Ingersoll and Liebenberg [30], for H_2 and N_2 as a function of wavelength

	Molecular hydrogen				Molecular nitrogen	
λ/Å	This work	Bishop and Cybulski [63]	Langhoff [55]	Martin et al. [45]	This work	Langhoff [55]
9875.0	0.9643	0.9684	0.9616	1.058	0.6636	0.6561
8500.0	0.9552	0.9587	0.9539	1.045	0.6361	0.6288
8000.0	0.9482	0.9511	0.9479	1.037	0.6350	0.6272
7500.0	0.9380	0.9418	0.9370	1.028	0.6404	0.6327
7000.0	0.9351	0.9381	0.9339	1.024	0.6401	0.6329
6500.0	0.9452	0.9483	0.9452	1.035	0.6431	0.6362
6000.0	0.9526	0.9559	0.9526	1.045	0.6453	0.6384
5893.0	0.9520	0.9549	0.9513	1.045	0.6470	0.6399
5780.0	0.9501	0.9530	0.9498	1.043	0.6447	0.6375
5500.0	0.9480	0.9511	0.9476	1.040	0.6436	0.6371
5460.0	0.9479	0.9511	0.9480	1.040	0.6433	0.6352
5000.0	0.9527	0.9559	0.9522	1.047	0.6401	0.6348
4500.0	0.9468	0.9493	0.9442	1.046	0.6388	0.6311
4360.0	0.9437	0.9465	0.9421	1.036	0.6382	0.6296
4000.0	0.9480	0.9512	0.9486	1.041	0.6393	0.6330
3635.0	0.9542	0.9559	0.9552	1.054	0.6438	0.6361

this paper. The parameter r is "relatively" insensitive with respect to wavelength (see Table 10).

5. Discussion

The uncertainties in the results for isotropic dipole properties, evaluated using the constrained DOSD approach used in this paper, have been assessed previously [1, 12, 22] when only experimental values of R_λ (or S_{-2} in some cases) and $S_0 = Z$ were used as constraints. For properties that depend significantly [3, 10, 12, 66] on the spectral regions which dominate the constraints used in constructing the DOSD, namely S_k, L_k and I_k for $-4 \leqslant k \leqslant 1$, the uncertainty in the results are generally $\leqslant 2\%$ for $k = 1$ and $\leqslant 1\%$ for the other values of $k \leqslant 0$. The errors increase slowly from $\sim 1\%$ for $k < -4$ and for $k = 2$ are $\approx 3\%$ since they are dominated by uncertainties in the DOS input data used to construct the high energy portion of the DOSD. These error estimates apply (generally) for molecules for which reliable (experimental errors $\leqslant$ a few tenths of a percent) molar refractivity constraints, and a significant dipole oscillator strength data base, are available (for example H_2 and N_2). There can be exceptions to these estimates due to cancellation effects, depending on k and on the nature of the molecular spectrum, that can occur in the logarithmic dipole sums L_k [12]. Examples are discussed in Sect. 4.1.1 for H_2 and, as pointed out there, the results for the "high energy" ($k = 2$, 1 and even 0) isotropic dipole properties obtained here are preferred, relative to the earlier results of Zeiss et al. [1], since reliable "high photon energy" constraints are incorporated into the calculations reported in Sect. 4.1.

Based on our experience with isotropic dipole properties, and assuming the anisotropic constraints for H_2 and N_2 are reliable (errors $\leqslant .5\%$ for $k = -2, -1$, $\leqslant 1\%$ for $k = 1, 2$), the error estimates discussed above for the isotropic properties should apply, generally, to the anisotropic properties of H_2 and N_2 obtained in this paper (probably including the L_k exceptions mentioned previously). Indeed the uncertainties for the $k = 1$ and 2 properties will be less than indicated previously.

The agreement between our results for the dynamic polarizability $\alpha(\epsilon)$, and its anisotropy $\gamma(\epsilon)$ for H_2, as a function of wavelength, with the recent highly reliable *ab initio* calculations of Bishop and Cheung [17] and Rychlewski [18] is remarkable [Table 6] with the only significant difference occurring at the Lyman α wavelength for $\gamma(\epsilon)$ [the discrepancies between the *ab initio* results, and our value, are 3.8% and 7.1%, respectively]. A similar comment applies with respect to the Verdet constant calculations of Bishop and Cybulski [63], see Table 10. We emphasize, again, the importance of this *ab initio* calculation which does not rely on the Becquerel equation (15).

Our DOSD results for H_2 and N_2, reported in Sect. 4, are often the most reliable, and sometimes the only reliable or available, values for many of the molecular properties considered (especially for N_2). The importance of these dipole properties has been discussed briefly in Sect. 2. Also, for example, $S_{-3/2}$ and S_{-3} can be used to obtain lower and upper bounds, respectively, for van der Waals dipole-dipole dispersion energy coefficients [20, 67]. The anisotropic components of the dipole properties can be used to discuss the anisotropy of the properties as a function of k and molecule, see Sect. 2. Important examples are furnished by the parameters (I_1^ζ, S_1^ζ) and I_0^ζ that help determine the straggling and stopping, respectively, of fast charged particles in matter [22–26, 68–71]. Defining the relative anisotropy of a property P by $X(P) = (P^{\parallel} - P^{\perp})/P$, we obtain, from our recommended results of Sect. 4, $X(I_1) = -22.6\%$ and 3.6%, $X(S_1) = -22.9\%$ and -3.3%, and $X(I_0) = -21.7\%$ and -15.6%, for H_2 and N_2, respectively. These results suggest that the stopping of fast charged particles by H_2 and N_2 will depend significantly on the orientation of the molecules with respect to the beam of fast particles, whereas the anisotropy of fast charged particle straggling effects will be large for H_2 and relatively small for N_2. A recent polarization propagator calculation, carried out at the random phase approximation level by Dierckson et al. [72], for a number of the dipole properties of N_2 also indicates a signficant anisotropy in the stopping power of N_2.

The DOSD methods used in this paper are the only approaches capable of yielding reliable results for *all* the dipole properties of molecules, both isotropic and anisotropic. Other techniques, based on less input data, can be of variable reliability [2, 3, 9, 20, 22, 73]. In principle purely *ab initio* methods can be employed to calculate molecular dipole properties. In practice *ab initio* methods furnish accurate results only for small systems or for special cases; some of the *ab initio* results discussed in Sect. 4 provide good examples.

Clearly *ab initio* calculations of the anisotropic components of the dipole sums S_2, S_1 and S_{-1} are an important (potential) source of anisotropic (and isotropic) constraints. Accurate *ab initio* results for these dipole properties are not easy to obtain, even for moderately small molecules, but such calculations are tractable since they require only ground state molecular wave functions [23, 25]. The relevance of reliable *ab initio* calculations for these properties (and for S_{-2}^{ζ} if available), in conjunction with reliable isotropic DOSDs, is clear from their use in the construction of the $\perp$- and $\|$-DOSDs for H_2 and N_2 and in the evaluation of the corresponding dipole properties (Sects. 3 and 4 and [15]). As demonstrated in Sect. 4 and [15], another important source of anisotropic constraints are reliable experimental values of depolarization ratios [27] ($\varrho_v^T(\epsilon)$) coupled with accurate results for isotropic dipole polarizabilities.

In order to obtain reliable results for the anisotropic components of *all* the molecular dipole properties (i.e. for all k) for H_2 and N_2 and other molecules, through use of the constrained anisotropic DOSD technique discussed here and in [15], reliable results for the $k = -2(1)2$ constraints are required. The number of constraints can be reduced considerably if only properties sensitive to the lower photon energy regions of the DOSD are considered. Thus, for example, reliable results for the anisotropic components of the dipole-dipole dispersion energy can be obtained through the use of accurate $k = 0$, -1, and -2 (or ϱ_v^T) anisotropic constraints for the interacting molecules [15].

The recommended anisotropic dipole properties S_k^ζ obtained from the anisotropic components of the H_2 and N_2 DOSDs have been used to construct pseudo $\|$- and $\perp$-DOSDs for these molecules [15]. These are reasonably compact discrete representations of the original anisotropic DOSDs that can be used to readily evaluate anisotropic dipolar dispersion energy coefficients for the interaction of H_2 and N_2 with each other and with other species [15]. These pseudo-DOSDs also yield all the properties in this paper, through their pseudo-spectral expressions [2, 13, 15, 42, 43, 74], to well within their estimated uncertainties.

References

1. Zeiss GD, Meath WJ, MacDonald JCF, Dawson DJ (1977) Can J Phys 55:2080
2. Kumar A, Fairley GRG, Meath WJ (1985) J Chem Phys 83:70, and many references therein
3. Meath WJ, Margoliash DJ, Jhanwar BL, Koide A, Zeiss GD (1981) In: Pullman B (ed) Intermolecular forces. Reidel, Dordrecht, pp 101–115, and references therein
4. Jhanwar BL, Meath WJ, MacDonald JCF (1986) Radiat Res 106:288, and many references therein; (1983) Radiat Res 96:20
5. Margenau H (1931) Phys Rev 37:1425; (1939) 56:1000
6. Dalgarno A, Lynn N (1957) Proc Phys Soc A70:802; Dalgarno A, Kingston AE (1958) Proc Phys Soc 72:1053; (1959) 73:455; (1961) 78:607
7. Victor GA, Dalgarno A (1969) J Chem Phys 50:2535
8. Thomas GF, Meath WJ (1977) Molec Phys 34:113
9. Jhanwar BL, Meath WJ (1982) Chem Phys 67:185
10. Jhanwar BL, Meath WJ, MacDonald JCF (1981) Can J Phys 59:185; (1983) 61:1027
11. Jhanwar BL, Meath WJ (1984) Can J Chem 62:373
12. Kumar A, Meath WJ (1985) Can J Phys 63;417; (1985) Can J Chem 63:1616
13. Pazur RJ, Kumar A, Thuraisingham RA, Meath WJ (1988) Can J Chem 66:615
14. Kumar A, Meath WJ (1991) Molec Phys, in press
15. Meath WJ, Kumar A (1990) Int J Quantum Chem S24:501
16. Ford AL, Browne JC (1973) Phys Rev A7:418
17. Bishop DM, Cheung LM (1980) J Chem Phys 72:5125
18. Rychlewski J (1983) J Chem Phys 78:7252
19. Langhoff PW, Gordon RG, Karplus M (1971) J Chem Phys 55:2126
20. Zeiss GD, Meath WJ (1976) Molec Phys 33:1155
21. Alms GR, Burnham AK, Flygare WH (1975) J Chem Phys 63:3321
22. Zeiss GD, Meath WJ, MacDonald JCF, Dawson DJ (1975) Radiat Res 63:64; (1977) Radiat Res 70:284
23. Hirschfelder JO, Byers Brown W, Epstein ST (1964) Adv Quant Chem 1:225

24. Dalgarno A (1966) In: Wilcox CH (ed) Perturbation theory and its applications in quantum mechanics. Wiley, New York, pp 145–183
25. Fano U, Cooper JW (1968) Rev Mod Phys 40:441; (1969) Rev Mod Phys 41:724
26. Inokuti M (1971) Rev Mod Phys 43:297
27. Bridge NJ, Buckingham AD (1966) Proc Roy Soc A295:334
28. Dalgarno A, Degges T, Williams DA (1967) Proc Phys Soc 92:291
29. Serber R (1932) Phys Rev 41:489
30. Ingersoll LR, Liebenberg DH (1956) J Opt Soc Am 46:538
31. Darwin CG, Watson WH (1927) Proc Roy Soc A114:474
32. Becquerel H (1897) CR Acad Sci 125:679
33. Huber KP, Herzberg G (1978) Constants of diatomic molecules. Van Nostrand Reinhold, New York
34. Mulder F, Meath WJ (1981) Molec Phys 42:629
35. Kolos W, Wolniewicz L (1964) J Chem Phys 41:3663
36. Ivanov AI, Rebane TK (1988) Opt Spectrosc 65:16
37. Meyer W (1976) Chem Phys 17:27
38. Wolniewicz L (1966) J Chem Phys 45:515
39. Kosman WM, Wallace S (1985) J Chem Phys 82:1385
40. Maroulis G, Thakkar AJ (1988) J Chem Phys 88:7623
41. Langhoff SR, Bauschlicher Jr CW, Chong DP (1983) J Chem Phys 78:5287
42. Margoliash DJ, Meath WJ (1978) J Chem Phys 68:1426
43. Margoliash DJ, Proctor TR, Zeiss GD, Meath WJ (1978) Molec Phys 35:747
44. Kumar A, Meath WJ, upon request
45. Martin PHS, Henneker WH, McKoy V (1975) J Chem Phys 62:69
46. Geertsen J, Oddershede J, Sabin JR (1988) Phys Rev A34:1104
47. Gerhart DE (1975) J Chem Phys 62:821
48. International Commission on Radiation Units and Measurements, Stopping Powers for Electrons and Positrons, ICRU Report No 37 (Bethesda, MD, 1984) p 21
49. Koch J (1912) Ark Mat Astr Fys 8:20
50. Kirn M (1921) Ann Physik 64;566
51. Smith PL, Huber MCE, Parkinson WH (1976) Phys Rev A13:1422
52. Gill P, Heddle DWO (1963) J opt Soc Am 53:847
53. MacAdam KB, Ramsay NF (1972) Phys Rev A6:898
54. Peck ER, Khanna BN (1966) J opt Soc Am 56:1059
55. Langhoff PW (1972) J Chem Phys 57:2604
56. Stroyer-Hansen T, Svendsen EN (1986) J Chem Phys 84:1950
57. Rowell RL, Aval GM, Barrett JJ (1972) J Colloid Interface Sci 39:472
58. Baas F, Van den Hout KD (1979) Physica 95A:597
59. Burnham AK, Buxton LW, Flygare WH (1977) J Chem Phys 67:4990
60. Belton MJS, McElroy MB, Price MJ (1971) Astrophys J 164:191
61. Wallace L (1972) Astrophys J 176:249
62. Dalgarno A, Williams DA (1962) Mon Not R Astron Soc 124:313
63. Bishop DM, Cybulski SM (1990) J Chem Phys 93:590
64. Cuthbertson C, Cuthbertson M (1909) Proc Roy Soc A83:151
65. Siertsema LH (1899) Arch neerl Sci 2:291
66. Zeiss GD, Meath WJ, MacDonald JCF, Dawson DJ (1980) Molec Phys 39:1055
67. Kramer HL (1970) J Chem Phys 53:2783; Pack RT (1970) Chem Phys Lett 5:257
68. Bischel H (1972) In: American Physics Handbook, 3rd ed. Sect 8d, McGraw-Hill, New York, pp 142–189
69. Fano U (1963) Annu Rev Nucl Sci 13:1
70. Bischel H (1974) Phys Rev A9:571
71. Mozumder A, LaVerne JA (1985) J Phys Chem 89:930
72. Diercksen GHF, Oddershede J, Paidarova I, Sabin J (1991) Int J Quant Chem 39:755
73. Mulder F, Meath WJ (1981) Molec Phys 42:629
74. Jhanwar BL, Meath WJ (1980) Molec Phys 41:1061