A simple semiempirical model for the static polarizability of electronically excited atoms and molecules

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We present a semiempirical analytical model for the static polarizability of electronically excited atoms and molecules, which requires very few readily accessible input data, including the ground-state polarizability, elemental composition, ionization potential, and spin multiplicities of excited and ground states. This very simple model formulated in a semiclassical framework is based on a number of observed trends in polarizability of electronically excited compounds. To adjust the model, both accurate theoretical predictions and reliable measurements previously reported elsewhere for a broad range of multielectron species in the gas phase are utilized. For some representative compounds of general concern that have not yet attracted sufficient research interest, the results of our multireference second-order perturbation theory calculations are additionally engaged. We show that the model we developed has reasonable (given the considerable uncertainties in the reference data) accuracy in predicting the static polarizability of electronically excited species of arbitrary size and excitation energy. These findings can be useful for many applications, where there is a need for inexpensive and quick assessments of the static gas-phase polarizability of excited electronic states, in particular, when building the complex nonequilibrium kinetic models to describe the observed optical refractivity (dielectric permittivity) of nonthermal reacting gas flows.

Keywords: polarizability, electronic excitation, semiempirical model, quantum chemistry

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1. Introduction

Electric properties of atoms, molecules, and clusters, which have been widely studied over the years,[1–4] continue to attract the attention of numerous research groups involved in different areas of atomic, molecular, optics, and chemical physics[5–26] as well as in relevant existing and emerging technological applications.[21,27–31] This is because the electric properties (primarily, dipole polarizability and, if present, permanent dipole moment) specify the variety of optical[1,32,33] and electrical[9,34–36] phenomena in molecular gases, underlie the theory of infrared and Raman vibrational spectra,[37] play a paramount role in intermolecular[11,19,23,38–41] and electron–molecular[42–44] interactions, and serve as markers of thermodynamic and kinetic stability of atomic/molecular systems.[24,25,40,45–53]

In this respect, it is not surprising that as a result of numerous experimental and theoretical efforts, a vast body of knowledge on the electric properties of atoms, molecules, atomic and molecular clusters has been gathered to date,[6–8,13,20,39,52–56] but most of these data refer to species in the lowest (ground) electronic states, predominantly populated at low (room) temperature, whereas disappointingly little is known about the effect of electronic excitation on the electrical response properties of multielectron systems. Meanwhile, appreciable electronic excitation of the gaseous components occurs both with thermal heating of gas to high temperatures (e.g., in thermal plasma) and under essentially nonequilibrium conditions relevant to post-shock[57–64] and expanding nozzle[60,61,65] flows, middle and upper layers of terrestrial and extraterrestrial atmospheres,[57,58,66–69] absorption of high-powered laser radiation in gaseous media,[16,57,70,71] electric discharge chemistry,[57,72–74] plasma-aided[78–83] and laser-induced[71,84] combustion.

Indeed, electric properties of atoms and molecules in excited electronic states are much less known and less studied (both experimentally and theoretically) than their ground-state counterparts[14,24,85–88] albeit these characteristics are of increasing interest for several distinctive issues, e.g., in the design of substances and (meta) materials with extreme nonlinear optical properties,[89–91] in understanding the solvatochromic shifts in electronic spectra,[86,91–93] in the interpretation of resonance energy transfer processes and molecular exciton interactions,[14] in optical (mainly, laser)[16,30,94,95] and microwave[96,97] diagnostics of nonequilibrium gas.

The precise knowledge of electric properties of atoms in highly excited electronic states is also an indispensable prerequisite for a number of promising applications based on the electromagnetic trapping of cold atoms (quantum metrology and quantum computing).[15,27,98–103] Besides, excited state electric properties enter the theoretical models of intermolecular and ion-molecule interactions involving excited colliding partners.[40,44,58,59] At long last, the basic electric properties of molecules in their excited electronic configurations gave essential information about the intrinsic features of the electronic structure of these excited states[87,91–93,104] and, accordingly,

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on the reactivity of electronically excited species.[45,46,48]

Importantly, the electric properties of atoms and molecules in the excited electronic states can be so different from those in the ground states[14,85–88,105–109] that the electronic excitation can markedly modify the electric, optical, and transport properties of gaseous media containing excited species and thus entail qualitatively new effects. For instance, electronic excitation of atoms and molecules when passing the intense laser radiation through the gas can lead to such peculiar phenomena as self-focusing of the laser beam due to the change in the refractive index of the medium.[33,70,110] Similarly, the appreciable abundance of electronically excited species significantly affects the propagation of radio waves both in nonthermal (low-temperature) and thermal plasmas.[111,112] Specifically, the knowledge of polarizability and dipole moment variation of species in excited states in comparison with the ground states is essential for analyzing electromagnetic wave propagation in low-temperature plasma in relation to the problems of the reliable operation of onboard instrumentation during spacecraft launching and reentry,[30,112] remote sensing of atmosphere,[113,114] and robust satellite-based location tracking.[113,115] In addition, enhanced polarizability of electronically excited states governs to some extent the reaction kinetics and molecular transport in thermal and nonthermal reacting gas flows.[109,116–119]

Consequently, it is highly important to know how the electric properties of a given multielectron system vary with its excitation to one or another electronic state. Note in this connection that whereas the ground state properties are routinely handled by the currently available quantum chemical machinery, the theoretical (in essence, computational) evaluation of electric properties of atoms and molecules in excited and, a fortiori, in highly excited electronic states continues to be a challenge to theory.[120–122] The point is that only a few of the standard electronic structure methods are generally capable of treating the electronic excitation,[123,124] and among those suitable methods for this purpose, there is no universally accurate technique to cope with all types of excitations and systems of all sizes.[21,122,125]

Specifically, a reliable *ab initio* description of excited electronic states requires, as a rule, abandoning the single-determinant assumption,[16,85,86,108,123,126] which is commonly used for the evaluation of molecular electric properties in the closed-shell ground states (see, e.g., Refs. [4, 6–8,13,17]). As a result, advanced but resource-demanding versions of the multiconfiguration (MC) self-consistent field (SCF) approach[16,85,86,93,108] that account for the multireference character of the wave function and electron correlation effects are generally employed for the accurate determination of static electric response properties of small and medium-size electronically excited molecules, and the computational requirements in this case dramatically increase with the number of the excited state in question. Alternatively, the equation-of-motion (EOM) coupled-cluster (CC) technique,[93,127,128] which is also rather computationally expensive, can be invoked for this purpose as well. However, in the last decades, for large systems with hundreds to thousands of atoms, where sophisticated wave-function-based quantum chemistry methods can hardly be implemented in common practice, the time-dependent (TD) density functional theory (DFT) approach has become the preferred method of choice for rough evaluation of the excitation energies and respective electric properties.[21,22,88,122] Unfortunately, this promising methodology is expected to work well only for states of certain types of excitation,[22,122,129,130] with the success of TD-DFT in the reliable estimation of the molecular electric properties depending heavily on the choice of the DFT functional.[21,22,87]

In light of the above, for diverse applications, especially, when constructing the complex nonequilibrium kinetic models with a large set of species, intended to precisely describe the observable optical refractivity (dielectric permittivity)[30,64,112,131] and transport properties[116–119] of nonthermal reacting gas flows, it would be highly convenient to have the simple theoretical tools that adequately predict the effect of electronic excitation on the polarizability and dipole moment (if present) of molecules and atoms. Such tools or analytical models would also be useful for critical evaluation of known and sometimes contradictory experimental and theoretical data on the electric properties of excited species.[14,22,88,108,132,133] This is especially true for high-lying electronic states, the difficulty of describing the electronic structure of which sharply increases with the excitation energy.[21,122,134,135]

Unfortunately, to the best of our knowledge, at the current state of the art in atomic and molecular physics, there is no model of this kind. Moreover, it is not clear on what principles such models can be based on, since at least, hitherto, the main trends in electric properties of electronically excited species have not yet been understood. However, more recently, an attempt has been made to summarize the known data on the influence of electronic excitation of atoms and molecules in the gas phase on their static dipole polarizability,[24] and preliminary considerations expressed there suggest that such a model can indeed be formulated in the framework of a semiclassical description at least for polarizability as a characteristic universally inherent in any multielectron systems, regardless of their symmetry properties.

Thus, the primary aim of this paper is to develop a physically reasonable and practical analytical model that would allow one to evaluate, on the basis of a minimal set of input data, the static gas-phase polarizability of electronically excited states both for atoms and arbitrary-sized molecules with

acceptable uniform accuracy.

Undoubtedly, since such an approximate model cannot but contain some empirical parameters, for its adjustment both accurate theoretical predictions and reliable measurements, previously reported elsewhere for a vast range of multielectron species, will be adopted. For some representative compounds of general interest that have not yet attracted much attention from researchers, we will additionally utilize the results of our *ab initio* calculations.

2. Assembling the data set for excited state polarizabilities

2.1. Analysis of the literature data

At the preparatory stage of the study, we had to compile a diversified and representative data set of reliable gas-phase polarizability values for atoms and molecules in excited electronic states that would allow one to investigate the regularities in polarizability of electronically excited species and adjust the semiempirical model to be developed. Note in this connection that since the polarizability values obtained by various theoretical methods are substantially dependent on the level of theory chosen,[4,6–8,17,20,132] it makes sense to represent the change in the static dipole polarizability due to electronic excitation in relative terms, i.e., via the ratio of the polarizability in the excited electronic configuration (with the energy relative to the ground electronic one T_e) to the ground state polarizability expressed as $\xi = \alpha(T_e)/\alpha(T_e = 0)$. In so doing, the errors in $\alpha(T_e)$ and $\alpha(T_e = 0)$ inevitably intrinsic to electronic structure calculations are at least partially compensated.

To begin with, the results of analytical[136,137] and numerical[106,138] calculations for H, C, N, O, Na, Si, P, S, and K atoms supplemented with recent experimental data for atomic Rb[99] were involved for this purpose. Then, we included in the fit data set the results of quantum chemical calculations performed under various multireference approximations for a number of small and medium-sized molecules (H_2, C_2, OH, CO, N_2, O_2, H_2O, HO_2, H_2S, O_3, CH_2O, C_2H_4, acetone)[16,24,93,104,108,109,132,133,139–141] and by using the EOM-CC approach for several quite large heterocyclic compounds (pyrimidine, s-tetrazine, uracil, and p-nitroaniline).[128,142]

Next, we used the potentially less accurate data obtained elsewhere in the single-determinant framework (SCF, DFT, and CC) for medium-sized and larger molecules (H_2, LiH, Li_2, C_2, N_2, LiN, F_2, HF, BF, NH, O_2, OS, S_2, H_2O, H_2S, CH_2O, C_2H_4, acetone, butadiene, pyrimidine, and benzonitrile)[87,93,107,108,129,132,133,143,144] and within the TD-DFT methodology for heterocyclic compounds (s-tetrazine, pyrimidine, pyridazine, pyridine, benzonitrile, uracil, and p-nitroaniline).[22,129] We also brought into play some results (for NO_2, O_3, benzene, naphthalene, anthracene, and pyrene) derived through the even less reliable single-excitation configuration interaction (CIS) calculations.[145–147] The ξ data obtained for several diatomics (LiH, Li_2, NaH, and CO) using less conventional techniques, such as the R-matrix with pseudostates (RMPS) method[148] and the time-dependent gauge invariant (TDGI) approach[149,150] were also included in the fit set. Finally, a number of experimental results for several molecules (O_2, benzene, naphthalene)[16,151,152] were involved into the analysis as well.

The meaningful data from the works cited above extracted for our purposes, namely, nomenclature for electronic states together with the respective T_e and ξ values, are summarized in the table of supplementary material. In total, the assembled data set includes the ξ literature values for different excited states of 46 species, with the number of data points exceeding 160 (for many atoms and molecules, there are data for several electronic states at once and, in addition, different data points can refer to the same excited state).

In point of fact, the data collected in this table are of very different origin and potential accuracy, and therefore it is hardly possible to expect their consistency even for the same electronic states. Indeed, even for the first excited state of hydrogen atom, the ratio of the fairly recent numerical quantum Monte Carlo polarizability estimate[138] to the analytical value by McDowell (1976)[136] reaches the value of 1.4. At once, for $5D_{3/2}$ and $5D_{5/2}$ levels of atomic Rb, the discrepancy between the results of analytical calculations[137] and magneto-optical trapping measurements[99] is about 10%. For molecules, the inconsistency in data from different sources can be even greater. So, for excited $H_2(B^1\Sigma_u^+)$, the ξ values calculated within the multireference (CASSCF method)[139] and DFT[107] frameworks differ almost twice.

In this regard, in order to correctly quantify the trends in electric properties of electronically excited species and, subsequently, to reasonably adjust the model to be developed, it makes sense to assign to the groups of data points obtained by using various methods the relative weights, which would in some way characterize the potential credibility of the data in use. The corresponding weights we set for each data point are also indicated in the table of supplementary material. As seen there, the analytically derived ξ values for hydrogen atom[136] were weighted ten times more than the somewhat obsolete results of single-reference SCF[133] and CIS[145] calculations for formaldehyde, ethylene, and butadiene. Accordingly, the reliability of data from other sources was voluntaristically rated on the scale from 1 to 10. Specifically, the ξ values calculated by using the second-order perturbation theory methods (XMC-QDPT2, CASPT2) and the EOM-CC technique were weighted by a factor of 6, whereas the TD-DFT based values were taken into account with a slightly lower weight equal to 4.

2.2. *Ab initio* calculations of this work

Unfortunately, despite the considerable amount of data on the polarizability of excited species accumulated to date, many practically important atoms and molecules (in particular, those that are abundant in atmosphere and combustion products) were not listed above in Subsection 2.1 due to the lack of available information. For that reason, to build a more balanced model for the effect of electronic excitation on the static polarizability of multielectron systems, we had to supplement the data set for excited state polarizabilities with the results of authors' own quantum chemical calculations performed for extra 10 species of general interest (He, F, Mg, Cl, CO_2, NO, and CH_x with $x = 1, \ldots, 4$). Besides, for Na, C_2, and S_2 species, whose excited state electric properties are difficult to describe (see, for example, Refs. [107,132,153]), we made additional calculations, the results of which duplicate the data declared in Subsection 2.1.

As a workhorse for static polarizability calculations in the present work, we employed the state-averaged CASSCF method[154] with flat weighting for the considered states[155,156] followed by the extended multiconfiguration quasi-degenerate second-order perturbation theory (XMCQDPT2)[157] calculations based on the CASSCF wave function as the reference state. This approach allowed us (i) to uniformly describe both the ground and excited states of interest making it possible to consistently determine the ratio of the polarizability in the excited electronic configuration to the ground state polarizability, and (ii) to take into account the effect of dynamic electron correlation, essential, in particular, for the description of excited state electric properties.[86,108] Throughout the work, either the general-purpose Dunning's correlation-consistent quadruple-zeta basis set with diffuse functions aug-cc-pVQZ[158] or its computationally less burdensome alternative specially developed for the accurate calculations of polarizability – the Sadlej's polarized triple-zeta basis set (Sadlej pVTZ)[159] – was used for multireference calculations.

For each electronic state of the given molecule, the equilibrium geometry was found by minimizing the electronic energy. Once this equilibrium configuration of atoms was determined, we performed finite-field polarizability calculations in terms of the energy expansion formalism.[160] The required quantum chemical calculations throughout the present work were conducted by Firefly QC program package[161] partially based on the GAMESS (US) source code.[162] The active space dimensions (the numbers of active electrons N and orbitals M) adopted for the multireference calculations of the excited electronic states of considered species, the basis set employed for this purpose, the obtained T_e and ξ values are provided in Table 1. The relevant data extracted from *ab initio* calculations of this work are also summarized in the table of supplementary material.

Table 1. Relative polarizability ξ of electronically excited states for a number of atomic and molecular species obtained *ab initio* in this work (together with the details of these calculations) as compared to the reference ξ_{ref} data.

Species	Excited state	N	M	Basis set	T_e (eV)	ξ	ξ_{ref}
He	2^3S	2	6	aug-cc-pVQZ	19.83	22.35	
	2^1S				20.85	19.98	
F	2^4P	5	12	Sadlej pVTZ	14.41	43.65	
	2^2P				15.20	64.31	
Na	2^2P	7	12	Sadlej pVTZ	2.11	1.52	2.19[137]
Mg	2^2P	2	13	Sadlej pVTZ	2.59	0.87	
	3^2P				4.31	3.04	
Cl	2^4P	7	13	Sadlej pVTZ	9.41	18.01	
	2^2P				10.00	22.09	
C_2[a]	$X^1\Sigma_g^+$	8	8	Sadlej pVTZ	0.05	0.38	0.62[132]
	$A^1\Pi_u$				1.02	1.08	
NO	$a^4\Pi$	11	8	aug-cc-pVQZ	4.57	1.26	
	$b^4\Sigma$				5.41	0.74	
	$B^2\Pi$				5.51	1.23	
S_2	$a^1\Delta_g$	12	8	Sadlej pVTZ	0.57	0.97	
	$b^1\Sigma_g^+$				0.98	0.96	1.00[107]
CO_2	$^3B_2$	16	12	Sadlej pVTZ	4.12	1.19	
	$^3A_2$				4.75	1.22	
	$^1A_2$				4.93	0.85	
CH	a^4S	5	9	Sadlej pVTZ	0.66	0.82	
	A^2D				2.99	1.03	
	B^2S				3.12	1.13	
CH_2	a^1A_1	6	10	Sadlej pVTZ	0.44	1.10	
	b^1B_1				1.57	1.12	
	c^1A_1				2.61	1.12	
CH_3	$3s\ ^2A_1'$	7	11	Sadlej pVTZ	5.44	21.03	
CH_4	^1A	8	8	Sadlej pVTZ	8.22	4.52	

[a]As a matter of fact, the singlet $X^1\Sigma_g^+$ state is commonly accepted as the lowest energy state of C_2 dimer, however our calculations gave the inverse arrangement of $X^1\Sigma_g^+$ and $a^3\Pi_u$ electronic states (in effect, the singlet-triplet energy gap is very small in this case).

As for the reliability of the results presented here, the following may be noted. Firstly, the multiconfiguration second-order perturbation theory methods, conceptually similar to the XMCQDPT2[157] one we employ, capture both electron correlation effects and the multireference character of the excited states and thus are considered to be reasonably accurate and, at the same time, not too computationally expensive in determining the polarizability of the ground-state[123,163–165] and electronically excited species.[93,106,108,123]

Secondly, the use of the XMCQDPT2 technique to describe the electric properties of excited species was conclusively justified in Ref. [16] by comparison with preceding theoretical estimates[104,107,118] and, more importantly, with experimental data for molecular oxygen obtained there employing the diagnostics by laser-induced gratings. With that, it was incidentally shown there[16] that the extended general purpose aug-cc-pVQZ basis set and the computationally cheaper Sadlej pVTZ one ensure very similar values for the relative polarizability ξ of O_2.

At last, a comparison of the ξ values we obtained for Na, C_2, and S_2 species with the literature data[107,132,137] further confirms the adequacy of the methodology used even in cases that are problematic for the electronic structure machinery.

Note also that the relative credibility weights equal to 6, the same as we took in Subsection 2.1 for the other second-order perturbation theory calculations, can be assigned to all the ξ values obtained by us.

3. Main regularities and model development

As is known,[85–87,105–108,140] for most atoms and molecules, their electronic excitation leads to the polarizability increase pronounced to a greater or lesser extent. Such enhancement in electric response of multielectron system is usually associated with the population of a more diffuse and electrostatically softer molecular orbitals.[87,93,104,108,128] Note also that these observations are consistent with the so-called minimum polarizability principle[50] (known in several formulations,[7,25,49–52] e.g., as applied to our case, stating that the more stable the electronic state, the less polarizable it is[48,107]).

To quantify this effect, we will adopt a semiclassical description, generally suitable for hydrogen-like and highly-excited atomic levels.[166,167] Within this framework, the excitation of a hydrogen-like atom to the nth electronic state (specified by the principal quantum number n) results in a growth of its static dipole polarizability asymptotically by $\sim n^6$ times[70,121,167] (indeed, classically, the polarizability of a conducting sphere is proportional to the cube of its linear scale,[26,168] whereas the spatial extent of the electron density in an excited atom varies as n squared[106]). The energy of the hydrogenic atom in the nth level, in turn, according to the Bohr–Rutherford model scales is n^{-2}.

Given these premises, it is easy to conclude that for the hydrogen-like atom with nuclear charge $Z = 1$, the ratio of the polarizability in the electronically excited state to the ground state polarizability is governed simply by

$$\xi_{\mathrm{H}} = \frac{1}{\left(1 - \frac{2T_{\mathrm{e}}}{E_{\mathrm{h}}}\right)^3}, \tag{1}$$

where E_{h} is the atomic unit of energy (27.211 eV). According to this expression, the polarizability of such an excited hydrogenic atom grows unrestrictedly with excitation energy T_{e}, formally tending to infinity as the excitation energy approaches the $E_{\mathrm{h}}/2$ threshold, which is nothing but the ionization potential of the hydrogen atom.

A relative increase in the static polarizability of a hydrogen-like atom with $Z = 1$ estimated by Eq. (1) is shown against the ratio of T_{e} to the ionization potential I_{p} in Fig. 1 as compared to the results of analytic solution by McDowell[136] (for H atom with $n = 2, \ldots, 10$) and numerical quantum Monte Carlo calculations by Li *et al.*[138] (for H atom with $n = 2$). From this plot we can see that the estimates using the very simple formula (1), based on the semiclassical considerations, are surprisingly well aligned with the results obtained with more accurate theoretical approaches.

In principle, the excited-state polarizability of any other multielectron component, not just the hydrogen-like atom, should behave qualitatively the same, i.e., increase indefinitely as T_{e} approaches the ionization threshold.[169,170] This provides a basis for generalizing Eq. (1) to any atomic or even molecular species by replacing half the atomic unit of energy with the corresponding first ionization potential of nonexcited component I_{p}. Hereby, the ratio of $\alpha(T_{\mathrm{e}})$ to $\alpha(T_{\mathrm{e}} = 0)$ for an arbitrary multielectron component can be stated in the form

$$\xi = \frac{1}{\left(1 - \frac{T_{\mathrm{e}}}{I_{\mathrm{p}}}\right)^{\gamma}}, \tag{2}$$

where the power exponent γ (equal to 3 for the semiclassical Bohr–Rutherford atom), following our recent supposition,[24] can be considered as the fitting variable of the model.

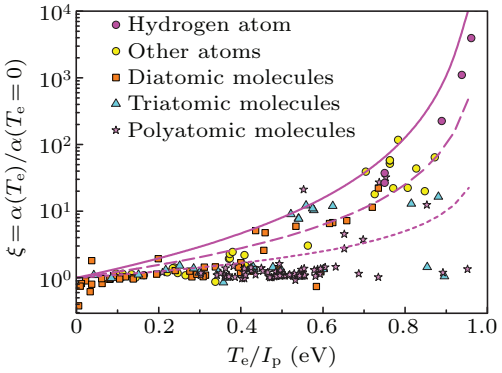


Fig. 1. The relative polarizability ξ of electronically excited atoms versus $T_{\mathrm{e}}/I_{\mathrm{p}}$ according to the semiclassical hydrogenic model provided by Eq. (1) (solid curve) or by Eq. (2) with $\gamma = 2$ and 1 (dashed and dotted curves) together with the ξ data for various atoms and molecules based on the measurements,[16,99,151,152] the analytical predictions,[136,137] and computational estimates performed in the present study and elsewhere[16,22,24,87,93,104,106–109,128,129,132,133,138–150] (symbols).

The need to adjust the dependence provided by Eq. (2) by varying γ becomes apparent when taking into account, in addition to the relative polarizability values for atomic hydrogen, the actual ξ data[16,22,24,87,93,99,104,106–109,128,129,132,133,137,139–152] for atoms of other elements as well as for different molecules additionally plotted in Fig. 1. We note, in passing, that the $T_{\mathrm{e}}/I_{\mathrm{p}}$ ratio, appearing in Eq. (2), is a nondimensionalized counterpart of T_{e} and is therefore useful as a kind of self-similar variable[171] for a uniform representation of the ξ data manifold.

Indeed, what we see is that while the proposed analytical scaling law given by Eq. (1) at least qualitatively reflects the overall trend for atoms and small (di- and triatomic)

molecules, as the number of atoms in a molecule increases, it fails to properly predict the $\xi(T_e)$ variation. As evinced by Fig. 1, the polarizability of electronically excited species grows with the T_e/I_p ratio (dimensionless electronic excitation energy) in general weaker than that of a semiclassical hydrogen-like atom, and for large polyatomics this growth is almost negligible. In terms of Eq. (2), this implies that the value of γ must be substantially reduced compared with the exponent in Eq. (1). To visualize this point, the dependences specified by Eq. (2) with fixed γ values equal to 2 and 1 are depicted in Fig. 1 as well.

Moreover, for some molecules, such as CH, C_2, O_2, S_2, and HO_2, the polarizability upon electronic excitation may even slightly decrease. To exemplify this point, let us consider in detail the case of O_2 molecule. As briefly noted in Subsection 2.2, the thorough multireference XMCQDPT2 polarizability calculations have been invoked relatively recently to find the static polarizabilities for the ground triplet ($X^3\Sigma_g^-$) and two excited singlet ($a^1\Delta_g$ and $b^1\Sigma_g^+$) electronic states of molecular oxygen.[16] It has been exhibited that the excitation of O_2 into the lowest singlet electronic states induces some reduction in its electrical response: the polarizabilities of delta and sigma states are smaller (by factors of 0.967 and 0.962, respectively) than that of $O_2(X^3\Sigma_g^-)$. This peculiarity of singlet dioxygen may be related to the fact that, unlike most other molecules, the excitation of molecular oxygen to the $a^1\Delta_g$ electronic configuration does not entail the population of a more diffuse, higher energy orbitals (the same is true for the $b^1\Sigma_g^+$ state as well).[104,123,140,172] Notably, this fact correlates with experimental evidence for the UV absorption transition intensities of O_2.[140] The calculated ξ value for the $b^1\Sigma_g^+$ state,[16] being qualitatively consistent with Williams' supposition put forward back in the late 1980s,[173] was also quantitatively confirmed experimentally by using the diffraction at laser-induced gratings[16] (more details of this technique can be found in Ref. [94]).

Now back to Fig. 1. The exact nature of the $\xi(T_e)$ dependence, as seen here, is not self-evident. However, as stated above, it is tempting to propose a model for γ that would adapt Eq. (2), originally written within the semiclassical picture for hydrogenic atom, to describe the influence of electronic excitation of arbitrary atoms and molecules on their static dipole polarizability in the gas phase. Let us also remark that the data presented in Fig. 1 are fairly evenly distributed along the abscissa axis, which allows us to hope that the model we are going to build by analyzing these data will be uniformly adequate for any T_e values.

Clearly, it is hardly possible to formulate any strict laws for energy and polarizability of arbitrary atomic or molecular species depending on the number of the electronic state (similar to those mentioned above for a hydrogen-like atom) that would allow one to analytically determine the γ value in each particular case. However, we can try to identify the meaningful factors governing the deviation of the "observed" γ values (i.e., when substituted into Eq. (2), corresponding to the given ξ value) from 3, and on this basis, staying within the physically sound and practical Eq. (2), to develop the desired model for the effect of electronic excitation on the static polarizability of multielectron systems.

Before we turn to a discussion of possible expression for γ, let us take a closer look at the form of Eq. (2). Given that the first ionization potential of the electronically excited component I_p^* is reduced relative to the ground state by the excitation energy, i.e., $I_p^* = I_p - T_e$, the structure of this expression is equivalent to the statement that the polarizability of excited compounds is inversely related to $(I_p^*)^\gamma$.

This scaling can be interpreted in some way as a generalization of a recognized theory-based regularity[174,175] observed for the ground electronic state atoms,[5,175–179] molecules,[180,181] atomic and molecular clusters.[182–184] Specifically, according to Refs. [175,178,179], polarizability of neutral atoms varies inversely with I_p^γ, where γ, depending on the completeness of the data set used for analysis and the accuracy of borrowed polarizability values, must be about 2.4–3.2. For molecules, the situation is qualitatively similar, but the exponent value providing the best fit of polarizability to a reverse power of I_p can be notably lower than that for atoms (γ ranges from 1 to 2).[180,181] Interestingly, an expression of this kind was recommended for approximate estimates back in 1937 by Hellmann in his pioneering book,[174] while the γ exponent was suggested to be 2 in all cases.

In fact, the existence of the negative correlation between α and I_p is not surprising and appears to be a manifestation of the intrinsic relationship between the polarizability (a measure of how readily the overall electronic charge distribution can be distorted by an external electric field) and the ionization energy of an atom or molecule (indicates how tightly bound is the most energetic electron).[177,179] Thus, Eq. (2), derived from semiclassical considerations, could alternatively be arrived at on the basis of the fundamental relationship between the ionization energy and the polarizability. This equivalence supports the validity of Eq. (2) we proposed, and the above-mentioned influence of the number of atoms (or rather, electrons) on the steepness of the $\alpha(I_p)$ dependence can be used as a basis of the model for γ.

Indeed, our preliminary analysis[24] has shown that, if Eq. (2) is used to interpret the data on ξ, the specific value of γ depends mainly on the size of a multielectron system. At first glance, the total number of electrons in the system N_{el} can be readily taken as a measure of size,[24] but instead we will use the sum of outer (valence) electrons N_{out} of atoms constituting this structure, because it is the number of outer electrons

that firstly specifies the polarizability of the system.[174,177,181] However, to correctly take into account the role played by the inner-shell electrons $N_{\rm inn}$ compared to that played by the outer-shell ones only, for the elements starting with Li, we propose using the effective number of outer electrons $N_{\rm out}^{\rm eff}$ introduced by Cambi *et al.*[168] as follows:

$$N_{\rm out}^{\rm eff} = N_{\rm out}\left[1+\left(1-\frac{N_{\rm out}}{N_{\rm inn}}\right)\left(\frac{N_{\rm inn}}{N_{\rm out}}\right)^2\right]. \tag{3}$$

For instance, in accordance with this expression, for Li ($N_{\rm out}=1$), C ($N_{\rm out}=4$), F ($N_{\rm out}=7$), Na ($N_{\rm out}=1$), and S ($N_{\rm out}=6$) atoms $N_{\rm out}^{\rm eff}$, it takes the values of 1.22, 3.56, 6.14, 1.74, and 6.94, respectively. Obviously, for the first row elements H and He, no correction is due and in the formula (3), $N_{\rm out}^{\rm eff}=N_{\rm out}=N_{\rm inn}$.

With the above in mind, it is interesting to look at the γ values that correspond to the data points presented in table of supplementary material and accordingly in Fig. 1. If Eq. (2) is used to describe them, the resulting γ values depend on the sum of the effective numbers of outer electrons of atoms that make up the compound $S_{\rm out}^{\rm eff}$. To this end, the observed $\gamma_{\rm obs}$ values provided by the $\ln(\frac{1}{\xi})/\ln(1-\frac{T_{\rm e}}{I_{\rm p}})$ ratio are plotted in Fig. 2 as a function of $S_{\rm out}^{\rm eff}$. For this purpose, the $I_{\rm p}$ values borrowed from the reference databases[55,186,187,187] were used.

We plainly see that the $\gamma_{\rm obs}$ values corresponding to the observed growth of polarizability with electronic excitation are quite close to 3 for very small systems, while with the increase in the number of outer electrons the effect of excitation on the polarizability sharply drops. Specifically, for large polyatomic compounds such as uracil, naphthalene, and pyrene, the $\gamma_{\rm obs}$ values are close to zero. At the same time, for some electronic states of a number of species (Mg, CH, C_2, NO, O_2, S_2, HO_2, and others), the $\gamma_{\rm obs}$ value can even go into the negative domain (i.e., $\xi<1$ for these species).

Following the objectives outlined above, it would be reasonable to approximate the visualized behavior for $\gamma_{\rm obs}$ by some suitable function of $S_{\rm out}^{\rm eff}$, for example, according to the recent suggestion,[24] by a simple power-law. However, as observed in Fig. 2 where this fit is additionally plotted, the scatter of data points about the fitting curve is exceedingly large. This implies that there must be other factors characterizing the enhancement in polarizability with electronic excitation.

Actually, along with the number of valence electrons, the number of atoms $N_{\rm at}$ can also be a significant factor affecting the mobility of electronic subsystem upon excitation. In other words, the steepness of the $\gamma_{\rm obs}(S_{\rm out}^{\rm eff})$ dependence can vary with $N_{\rm at}$. The fact that this seems to be true is visible in Fig. 2.

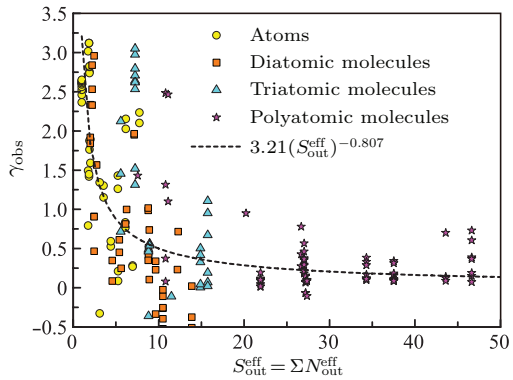


Fig. 2. The observed $\gamma_{\rm obs}=\ln(\frac{1}{\xi})/\ln(1-\frac{T_{\rm e}}{I_{\rm p}})$ values for the species presented in Fig. 1 against $S_{\rm out}^{\rm eff}$ (symbols) together with the power function fit to these data (dotted curve).

Next, despite the fact that the structure of Eq. (2) already includes a dependence on the excitation energy $T_{\rm e}$, the γ parameter itself may depend on $T_{\rm e}$. Thus, we found that for different electronic states of the same component, the observed $\gamma_{\rm obs}$ values generally increase with $T_{\rm e}$. This tendency is illustrated in Fig. 3, where the $\gamma_{\rm obs}$ data extracted for a series of electronic states of H,[136] K,[137] Rb,[137] CH_2O (formaldehyde),[133] $C_4H_4N_2$ (pyrimidine),[22] C_7H_5N (benzonitrile),[87] $C_4H_4N_2O_2$ (uracil)[22] are plotted against the $T_{\rm e}/I_{\rm p}$ ratio. Qualitatively, this is expected, since with $T_{\rm e}$ growth, the resulting electric field, in which the outer electrons of multielectron atom or molecule move, becomes increasingly similar to a Coulomb field of a hydrogen-like atom.[166]

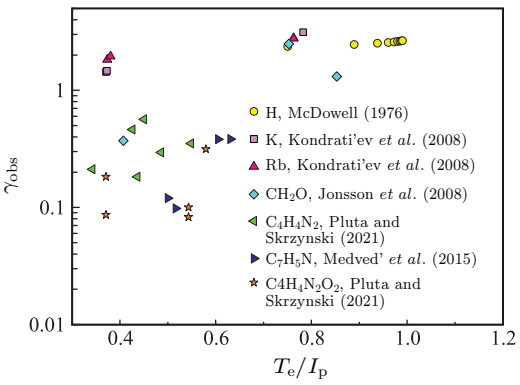


Fig. 3. The observed $\gamma_{\rm obs}=\ln(\frac{1}{\xi})/\ln(1-\frac{T_{\rm e}}{I_{\rm p}})$ values for different electronic states of some atomic and molecular species (see text) against the $T_{\rm e}/I_{\rm p}$ ratio (symbols).

Further, the spin multiplicity of electronic states in some way characterizes their polarizability, especially at low excitation energies $T_{\rm e}$.[107,128] Particularly, the open-shell systems can be more polarizable than their closed-shell counterparts of comparable $T_{\rm e}$ values.[16,107,132,143,144,149]

At last, the theory-based[174,175] and empirically observed[175–184] negative correlation between polarizability and ionization potential, discussed above, can also be incorporated into the expression for γ.

Based on the foregoing, we have tried to come up with a not too cumbersome function for γ that best describes the

available data set. After several trials, close scrutiny and numerical experiments led us to the 7-parameter expression for the γ exponent given by

$$\gamma = p_0 \frac{N_{\mathrm{at}}^{p_1}}{(S_{\mathrm{out}}^{\mathrm{eff}})^{(p_2+p_3\ln(N_{\mathrm{at}}))}} \times \left[\left(\frac{T_{\mathrm{e}}}{I_{\mathrm{p}}}\right)^{p_4} + p_5 2\Delta S \left(\frac{I_{\mathrm{p}}}{T_{\mathrm{e}}}\right)^2\right]\left(\frac{E_{\mathrm{h}}}{I_{\mathrm{p}}}\right)^{p_6}, \quad (4)$$

where $p_0, \ldots, p_6$ are dimensionless fitting parameters, T_{e} is the energy of a given excited electronic state with respect the ground one, I_{p} is the first ionization potential of the non-excited compound in question, E_{h} is the atomic unit of energy, and ΔS is the difference in the electronic spin of a given excited state and the corresponding ground one (note that the doubled ΔS is nothing but the difference in spin multiplicities). As seen, the structure of this expression includes only either dimensionless quantities (numbers of atoms and outer electrons, spin numbers) or dimensionless ratios of dimensional ones ($T_{\mathrm{e}}/I_{\mathrm{p}}$ and $E_{\mathrm{h}}/I_{\mathrm{p}}$). It is also remarkable that the power-law nature of the dependences incorporated into Eq. (4) is partly motivated by the previous methodologically similar studies.[5,181]

Thereby, our model for dependence ξ on T_{e}, consisting essentially of Eqs. (2) and (4), requires, apart from the excitation energy itself, very few input data: the first ionization potential, number of atoms, elemental composition (in order to determine $S_{\mathrm{out}}^{\mathrm{eff}} = \sum N_{\mathrm{out}}^{\mathrm{eff}}$), and spin multiplicities. The specific values of $p_0, \ldots, p_6$ parameters can be obtained by fitting to the compiled data set described in Section 2.

It should be stressed that, when constructing the model for predicting the effect of electronic excitation on the polarizability of molecules and atoms, we tried to propose an analytical expression that would not demand any specific knowledge of the electronic structure of excited systems, but would require setting only the well-defined and readily accessible properties of the ground state species.

Perhaps, the known data could be better fitted by significantly complicating the function initially provided by Eq. (2), introducing extra atomic or molecular properties as arguments in Eq. (4), and further increasing the number of fitting parameters. In particular, we have tried to somehow integrate into the model for γ such seemingly relevant quantities as the permanent dipole moment and electron affinity, but our attempts have not been successful. Virtually, we were unable to find other physically consistent functional forms that have a similar number of freely adjustable parameters and appreciably improve the quality of the fit compared to Eq. (2) supplemented with Eq. (4).

4. Results of the model adjustment and discussion

To find the $p_0, \ldots, p_6$ fitting parameters values [entering Eq. (4) for the effective variable γ] that provide the best performance of the model over the entire range of ξ, the diversified and representative fit data set was assembled as described in Section 2. It includes, aside from 168 literature data points for 46 individual species based on the trustworthy measurements[16,99,151,152] and theoretical estimates reported previously,[16,22,24,87,93,104,106–109,128,129,132,133,136–150] the results for 10 extra species of general interest (27 data points) obtained in our XMCQDPT2 finite-field polarizability calculations (see Table 1). The complete list of data points used for optimization (overall, 195 items) is available in supplementary material.

For all the compounds, we collected the atomic and molecular properties required to calculate the fitting exponent γ according to Eq. (4) and the relative polarizability ξ via Eq. (2) (also see supplementary material for more details). Specifically, the I_{p} values were taken from the relevant reference databases.[55,185,186] In the absence of the excitation energies T_{e} for some electronic states in the source papers for ξ cited above, we borrowed the necessary data from Refs. [188–192].

As discussed in Section 2, in order to configure the model we developed, it is reasonable to take into account the potential reliability of the collected data. In doing so, we used the weighted root-mean-square deviation (RMSD) error as metrics to assess a quality of the fitting (recall that the corresponding weights set for each data point are also given in the table of supplementary material).

Since the approximated quantity ξ can vary by a few orders of magnitude (see Fig. 1), throughout the fitting, the weighted RMSD of decimal logarithms of target values was minimized. Particularly, the $\lg(\xi)$ values adopted for the same electronic state from different sources were taken into account with their own weights.

In Table 2 are listed the resulting values of fitting parameters giving the best match of the predictions using the model [consisting essentially of Eqs. (2) and (4)] to the ξ data from the table of supplementary material. As seen, all parameters have reasonable magnitudes virtually matching the observed trends. For instance, the optimized p_0, p_1, and p_3 values, when inserted into Eq. (4), provide for $N_{\mathrm{at}} = 2$ or 3 roughly the same $\gamma(S_{\mathrm{out}}^{\mathrm{eff}})$ behavior as the power function fit depicted in Fig. 2.

Table 2. The obtained set of dimensionless fitting parameters.

p_0	p_1	p_2	p_3	p_4	p_5	p_6
2.225	0.789	0.097	0.489	0.605	0.00097	0.253

The approximated ξ values obtained by using the developed model are compared in Figs. 4(a) and 4(b), where they are plotted against T_e, with the corresponding magnitudes from the compiled data set. One can observe that while the relative polarizability ξ of electronically excited states behaves extremely nonmonotonically with T_e, the application of Eqs. (2) and (4) with the optimized $p_0,\ldots,p_6$ values enables to correctly track the dependence of ξ on T_e and other parameters that specify the effect of electronic excitation on the polarizability of molecules and atoms.

Looking at Fig. 4, we can also conclude that the present model, in view of the significant scatter in the reference data from various sources mentioned in Subsection 2.1, actually describes well the known ξ data at any T_e, although several data points for high-lying (T_e = 6–11 eV) electronic states of H_2O, O_3, C_2H_4, and CH_2O molecules, based on quantum-chemical calculations using not very reliable CASSCF, CIS, and SCF techniques,[108,133,146] lie away from the approximation curve we arrived at. In particular, the worst outlier is the SCF prediction[133] for a relatively high-lying (T_e = 9.65 eV) 1^1B_1 state of formaldehyde, for which Jonsson *et al.*[133] gave, oddly enough, a very small polarizability value (more 13 times less than our model yields).

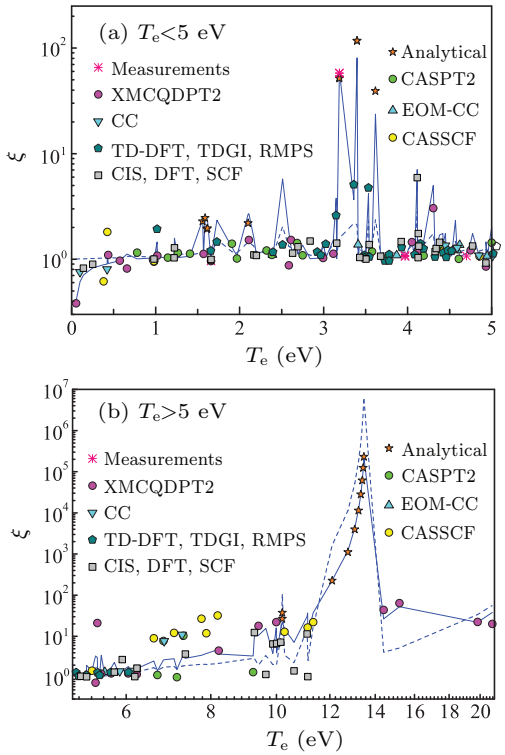


Fig. 4. The ξ value for various species as a function of T_e: available experimental and theoretical data from the fit data set (symbols) and approximations using the developed (jagged solid line) and previously proposed[24] (jagged dotted line) models.

It would also be interesting to compare the performance of the present model with the accuracy in ξ provided by the expression for the γ parameter we previously proposed in Ref. [24], when substituted into Eq. (2). Thus, according to Ref. [24], the exponent in Eq. (2) can be expressed via the number of electrons in the system N_{el} as

$$\gamma = 3.36 N_{el}^{-0.65}. \tag{5}$$

The ξ values estimated in this way are additionally plotted in Fig. 4. We can see that, while an approximation based only on the number of electrons[24] qualitatively reflects the general $\xi(T_e)$ dependence, it is significantly inferior in accuracy to the model of this work. So, the value of coefficient of determination (R^2) (calculated in line with the recommendations[193]) for the $\lg(\xi)$ values as provided by Eq. (5) (from Ref. [24]) with respect to the literature data is appreciably lower (R^2 = 0.728) than when using the model we developed in this work (R^2 = 0.937).

Interestingly enough, the analytical tool we developed to predict the effect of electronic excitation on the polarizability works best for atoms, whereas, as the size of the system in question increases, its accuracy has somewhat deteriorated. This is clearly seen from Table 3, which lists the respective R^2 values for the whole fitting data set as well as for mono-, di-, and polyatomic species separately. In general, this trend is not surprising, since our model consisting Eqs. (2) and (4) was initially inspired by semiclassical $\xi(T_e)$ dependence for the hydrogen-like atom given by Eq. (1), and as the electronic structure becomes more complex, the response of an electron cloud to an external electric field is expected to be worse described by the algebraic expressions we proposed.

Table 3. The coefficient of determination R^2 for the $\lg(\xi)$ values calculated using the present and previous[24] models with respect to the reference data for the whole fitting set as well as for its subsets.

Subset	Eq. (3)	Eq. (5)
Entire set	0.937	0.728
$N_{at} = 1$	0.993	0.654
$N_{at} = 2$	0.673	0.734
$N_{at} > 2$	0.418	0.306

Lastly, let us evaluate the predictive power of the worked out model, namely, how it performs outside the data set for excited state polarizabilities used to find the $p_0,\ldots,p_6$ fitting parameter values. For this purpose, the additional ξ data[15,22,102,120,126,133,194–196] for some atoms (Be, Mg, Zn, Rb, Cd, Yb, and Hg) and molecules (cyclobutadiene, pyrazine, thymine, and cytosine), accidentally not introduced into the fitting procedure described above (overall, 26 data points), are to be confronted with the corresponding values predicted by using the configured model. Figure 5 provides such a comparison, plotting against T_e the ξ model predictions together with the corresponding literature data. One can see that our model performs rather well for species for which it has not been tuned, and the R^2 value for this kind of test set (0.991) is very close to that obtained for the fitting set (see Table 3).

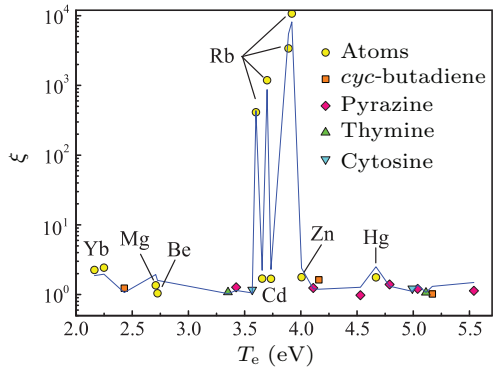


Fig. 5. Comparison of ξ predictions using the present model (polyline) with the reference data[15,22,102,120,126,133,194–196] (symbols).

5. Concluding remarks

The principal finding of the present work that we would like to stress is a very simple analytical model of semiempirical origin for predicting the static polarizability of electronically excited atoms and molecules in the gas phase. To determine the relative increase in the static polarizability upon electronic excitation, a couple of two plain expressions can be used: (i) Eq. (4) for the effective variable γ governing within the semiclassical description the degree of influence of electronic excitation on the polarizability and (ii) Eq. (2) that provides for a given effective variable the desired ratio of the polarizability in the excited electronic configuration to the ground state polarizability.

This model is based on the semiclassical considerations and on a number of more or less substantiated regularities in polarizability of electronically excited compounds. The presence of free parameters in the derived model enabled us to adjust it to match the known body of data on the polarizability of atoms and molecules in their excited electronic states. To this end, relying on the theoretical predictions and measurements reported previously, we assembled a diversified set of gas-phase polarizability values of 46 monatomic and polyatomic species in excited electronic states (overall, 168 data points). For extra 10 species of general interest, for which no literature data are available, we additionally carried out our own second-order perturbation theory calculations (in this way, another 27 data points were obtained).

In the long run, the simple semiempirical model we developed has reasonable (given the considerable uncertainties in the reference data) accuracy in predicting the static polarizability of electronically excited species of any size and excitation energy. It requires, apart from the excitation energy itself and the spin multiplicities of excited and ground states, only very few readily accessible properties of the ground state compounds to be specified (first ionization potential and elemental composition), leaving aside the knowledge of the electronic structure specifics in excited systems.

We suppose that the worked out model is accurate enough for diverse applications where there is a need for quick low-cost estimate of the effect of electronic excitation on the polarizability of a large set molecules and atoms. The developed tool can also be useful for critical evaluation of known and sometimes contradictory experimental and theoretical data on the electric properties of excited species.

In conclusion, we note that the analytical model constructed in the present work does not claim to be final and complete. It is ready for further recalibration based on dependable past data that we unfortunately overlooked and additional theoretical or experimental evidence that may become available in the future. Likewise, when using new additional data, some revision of the underlying premises and, accordingly, reconfiguration of the model are also not ruled out.

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