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Dynamic scalar and tensor polarizabilities of the $2\,^1P$ and $2\,^3P$ states of He

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The dynamic dipole polarizabilities at real and imaginary frequencies have been determined for the helium atom in its lowest singlet and triplet $2P$ states, using our time-dependent gauge-invariant method. Contributions of the $2S$ states to static polarizabilities are strong and negative, particularly in the case of the singlet $2\,^1P$ state, for which the static scalar polarizability α_0 is negative. The tensor polarizability α_2 corresponding to the differential Stark shift between the m-Zeeman sublevels was also calculated and compared to previous theoretical and experimental results for the singlet $2\,^1P$ state. An evaluation of the C_6 dispersion coefficients for the $2\,^1P$–$2\,^1P$ and $2\,^3P$–$2\,^3P$ systems is also given, derived from the dynamic polarizabilities at imaginary pulsations ω.

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I. INTRODUCTION

Collision processes involving excited atoms play an important role in such fields as gas lasers and plasma physics. In relatively high-pressure gases, even optically allowed excited states become as important as metastable states in spite of their short lifetimes, since collision times become shorter than these lifetimes. In this way, deexcitation of excited rare-gas atoms by various target molecules is very important in both basic and applied chemical physics studies [1–3], in particular modeling reactive plasmas. Because of experimental difficulties using crossed beam [4,5], heightened interest in the calculation of Penning ionization cross sections recently appeared for collisional ionization by a resonant state atom such as He ($2\,^1P$) [6–9]. These semiclassical [7–9] and quantum-mechanical [6] calculations are carried out using long-range interaction-potential models involving knowledge of the dipole polarizability for the resonant atom, and an estimation of the Van der Waals parameter.

Progress has been made in recent years in theoretical calculations of dynamic polarizabilities of atoms in their ground and excited states. These studies concern essentially the metastable or resonant states of a two- or three-electron system such as $2\,^1S$ and $2\,^3S$ states of He [10–13] and Li$^+$ [11,12], $2\,^4P$ states of He$^-$ and Li [14], and the $2\,^3P$ doubly excited state of the prototype negative ion H$^-$ [15]. Generally, when the excited states are the lowest low-lying states, the values of dynamic polarizabilities for real pulsations ω are positive and increase until the first resonance [10–14]. When a resonant ($2\,^1P$ and $3\,^1P$ states of He) [9,16] or a second bound state ($2\,^3P$ state of H$^-$) [15] is concerned, the behavior of the dynamic polarizabilities may be different.

The aim of this paper is to present accurate calculations of the dynamic (both real and imaginary frequencies) dipole polarizabilities for two states ($2\,^1P$ and $2\,^3P$) of He. As in the case of the $2\,^1S$ and $2\,^3S$ states [10], our time-dependent gauge-invariant (TDGI) method [17] is used. When possible, our scalar $\alpha_0(\omega)$ and tensor $\alpha_2(\omega)$ values for polarizabilities of the $2\,^1P$ state are compared to the experimental results of Bhaskar and Lurio [16], using an electric-field level-crossing technique, and with their theoretical static values evaluated from a sum over about ten discrete states, using the oscillator strengths of Green *et al.* [18]. Concerning the $2\,^3P$ state our results are original.

II. THEORETICAL AND COMPUTATIONAL DETAILS

Scalar α_0 and tensor α_2 polarizabilities for the $2\,^1P$ and $2\,^3P$ states are calculated using the definitions in [14]:

$$\alpha_0 = (\alpha_{10} + \alpha_{11} + \alpha_{12})/9$$

and

$$\alpha_2 = -(\alpha_{10} - \tfrac{1}{2}\alpha_{11} + \tfrac{1}{10}\alpha_{12})/9$$

in which α_{10}, α_{11}, and α_{12} are the contributions of the S, P and D states, respectively, to the polarizability of a P state. The basic means for obtaining reliable values of these components in the calculation of dynamic polarizabilities is to generate wave functions leading to accurate energies for the ground $1\,^1S$ and excited $2\,^1S$, $2\,^3S$, $2\,^1P$, $2\,^3P$, $3\,^1D$, and $3\,^3D$ states, as well as accurate dipole transition moments. In the case of $2P$ states (singlet and triplet) for which the corresponding energy levels are just above that of the $2S$ ($1s2s$) states and not much below that of the $3S$ ($1s3s$) and $3D$ ($1s3d$) states, it is very important to furnish an accurate description of these spectral states in order to account for resonances.

In our calculations, symmetry considerations as explained by Bauschlicher and Taylor [19] enable the problem to be reduced to one of the representing degenerate $2P$ states ($1s2p_x$, for example), whose polarizability components are related to α_0 and α_2 by $\alpha_{xx} = \frac{1}{3}\alpha_{10} + \frac{2}{15}\alpha_{12}$ and $\alpha_{zz} = \frac{1}{6}\alpha_{11} + \frac{1}{10}\alpha_{12}$ leading to $\alpha_0 = \frac{1}{3}(\alpha_{xx} + 2\alpha_{zz})$ and $\alpha_2 = \frac{1}{3}(\alpha_{zz} - \alpha_{xx})$.

In the same way, only the $1s3d_{xz}$ representation is considered when describing the $3D$ state, with the result that oscillator strengths between the P and D states are expressed by

$$\begin{aligned} f_{P\rightarrow D} &= 2\langle P|\mu|D\rangle^2 \Delta E \\ &= \frac{2}{3}\Delta E(\langle p_x|x|d_{z^2}\rangle^2 + \langle p_x|x|d_{x^2-y^2}\rangle^2 \\ &\quad +\langle p_x|y|d_{xy}\rangle^2 + \langle p_x|z|d_{xz}\rangle^2) \\ &= \frac{2}{3}\Delta E\frac{10}{3}\langle p_x|z|d_{xz}\rangle^2 \ , \end{aligned}$$

where $\Delta E = E_{3D} - E_{2P}$.

The α_{xx} and α_{zz} values are obtained from our variation-perturbation TDGI method developed elsewhere, which uses a first-order wave function combining a polynomial function and both true spectral and quasispectral series [17,20]. For α_{xx}, the spectroscopic states $2S$, $3S$ and $2P$ are calculated in addition to the pseudostates to obtain the first resonances $\hbar\omega = -(E_{2S} - E_{2P})$ and $\hbar\omega = E_{3S} - E_{2P}$. For α_{zz}, in addition to the P contributions (α_{11} terms), taken only into account in the pseudostates (the first active $2p_x 2p_z$ configuration being very high in energy), the D contributions are both described by a quasispectral series and the spectral $3D$ state leading to the first resonance $\hbar\omega = E_{3D} - E_{2P}$.

With the basis set described elsewhere [10], full configuration interaction (CI) calculations were carried out to obtain the ground and excited states of He using the multireference second-order many-body perturbation via the CIPSI algorithm [21,22]. The quality of our wave functions is illustrated by a comparison of our energies [10] with the exact nonrelativistic values. As an additional test of the accuracy and completeness of our wave functions, we calculated transition energies and oscillator strengths. As can be seen in Table I, there is excellent agreement between our theoretical values and the experimental data [23], enabling accurate static and dynamic polarizabilities for the $2\,^1P$ and $2\,^3P$ states of He to be expected.

Since there is a sign change of $\Delta E_{2P\rightarrow i}$ transition energies, it is no longer possible to use the Casimir-Polder integral formula [24,9] linking the van der Waals C_6 coefficient between two atoms in the same state to the dynamic polarizabilities for imaginary frequencies [$C_6 = \frac{3}{\pi}\int_0^\infty \alpha_0(i\omega)^2 d\omega$]. We can, however, use the $\alpha_0(i\omega)$ continuous function [rather than the $\alpha_0(\omega)$ discontinuous function] in order to fit a limited sum over states function [$\sum_i f_{2P\rightarrow i}/(\Delta E^2_{2P\rightarrow i} + \omega^2)$] where the $f_{2P\rightarrow i}$ oscillator strengths and $\Delta E_{2P\rightarrow i}$ transition energies are the fitting parameters. Taking the values of the first oscillator strengths and transition energies given in Table I ($f_{2P\rightarrow nS} = -f_{nS\rightarrow 2P}/3$) as the starting point of our optimization, the C_6 coefficient can now be written as the limited sum

$$C_6 = \frac{3}{2}\sum_{i,j}\frac{f_{2P\rightarrow i}f_{2P\rightarrow j}}{\Delta E_{2P\rightarrow i}\Delta E_{2P\rightarrow j}(\Delta E_{2P\rightarrow i} + \Delta E_{2P\rightarrow j})} \ .$$

To test this procedure, we can check the following equality obtained when the basis set is complete (n_e is the number of electrons):

$$\frac{1}{2}\sum_i \frac{f_{2P\rightarrow i}}{\Delta E_{2P\rightarrow i}} = \langle 1s2p_x|\sum_{l,m=1}^{n_e} x_l x_m + 2z_l z_m|1s2p_x\rangle \ ,$$

where the mean values of the bielectronic operators $(x_l x_m + 2z_l z_m)$ over the $2P$ states are relatively easy to calculate.

TABLE I. Comparison between calculated and experimental transition energies ΔE and oscillator strengths f_{ik} involving $1\,^1S$, $2\,^1S$, $2\,^3S$, $2\,^1P$, $2\,^3P$, $3\,^1S$, $3\,^3S$, $3\,^1D$, and $3\,^3D$ states of He. Experimental values are in parentheses (see text).

Transition	ΔE (a.u.)	f_{ik}
$1\,^1S \rightarrow 2\,^1P$	0.77888	0.272
$1s^2$ $1s2p$	(0.77975)	(0.276)
$2\,^1S \rightarrow 2\,^1P$	0.02225	0.380
$1s2s$ $1s2p$	(0.02213)	(0.376)
$2\,^3S \rightarrow 2\,^3P$	0.04214	0.541
$1s2s$ $1s2p$	(0.04206)	(0.539)
$2\,^1P \rightarrow 3\,^1S$	0.06393	0.056
$1s2p$ $1s3s$	(0.06256)	(0.048)
$2\,^3P \rightarrow 3\,^3S$	0.06491	0.074
$1s2p$ $1s3s$	(0.06447)	(0.069)
$2\,^1P \rightarrow 3\,^1D$	0.06880	0.693
$1s2p$ $1s3d$	(0.06821)	(0.711)
$2\,^3P \rightarrow 3\,^3D$	0.07821	0.590
$1s2p$ $1s3d$	(0.07753)	(0.609)

III. SCALAR AND TENSOR POLARIZABILITIES

The dynamic α_0 and α_2 values of the singlet $2\,^1P$ and triplet $2\,^3$P states of He are listed in Table II. The unusual negative static α_0 value obtained for $2\,^1P$ shows that, on average, this state is even more unstable in an electric field. The static α_2 value calculated for this singlet state, 224.4 a.u. or 3.326×10^{-23} cm^3, compares very well with the experimental value of $(3.32\pm0.10)\times10^{-23}$

TABLE II. Dynamic dipole polarizability of the $2\,^1P$ (S) and $2\,^3P$ (T) states of He. All results are in a.u.

ω	$\alpha_0^{(S)}$	$\alpha_2^{(S)}$	$\alpha_0^{(T)}$	$\alpha_2^{(T)}$
0	−59.84	224.4	49.50	67.09
0.005	−72.50	237.8	48.71	68.30
0.010	−120.8	288.5	45.99	72.28
0.015	−264.2	436.2	40.37	80.08
0.0175	−462.7	637.6	36.06	85.85
0.020	−1120	1299	30.13	93.51
0.025	1199	−1012	10.95	117.1
0.0275	715.7	−522.9	−5.065	135.8
0.030	551.3	−352.0	−29.16	163.0
0.035	432.3	−216.1	−138.9	280.5
0.0375	410.8	−183.9	−291.4	437.7
0.040	402.1	−162.3	−814.9	966.6
0.045	412.5	−138.1	948.9	−783.4
0.0475	430.8	−132.7	613.5	−439.5
0.050	459.5	−131.2	504.6	−320.3
0.055	566.0	−143.1	451.5	−240.1
0.060	839.9	−210.5	515.1	−261.5
0.0625	1277	−414.4	663.2	−378.5

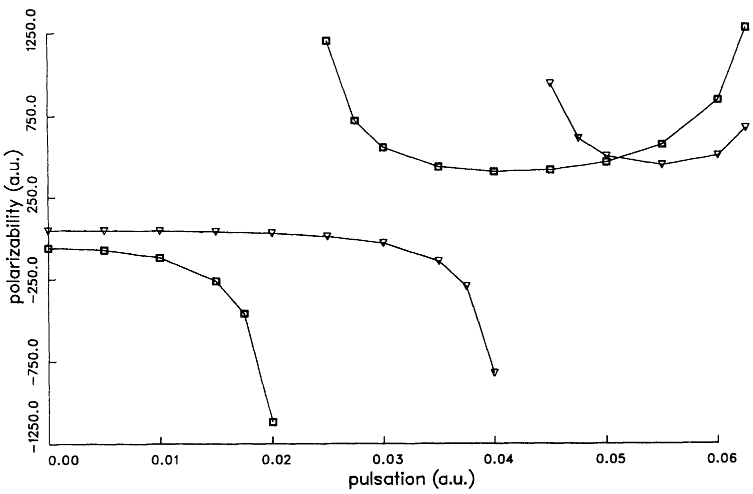

FIG. 1. Dynamic scalar polarizabilities of the singlet (squares) and triplet (triangles) $2P$ states of He versus real pulsations.

cm^3 [16]. It also agrees with the theoretical result obtained from a sum over about ten discrete states: $(3.34 \pm 0.06) \times 10^{-23}$ cm^3 [16].

Using the several oscillator strengths also given in [16] and in [23] for the singlet case, the static α_0 value can be found. These values, -69.5 and -67.7 a.u., are very different from ours (-59.84 a.u.). For the triplet case, our static α_0 value ($+49.50$ a.u.) also differs from those calculated using the oscillator strengths given in [23] ($+37.6$ a.u.). This discrepancy is therefore due to the positive contributions of the other discrete states and to the continuum taken into account in our calculation of $\alpha_0 = \frac{1}{3}(\alpha_{xx} + 2\alpha_{zz})$. It should be stressed that the similarity of the values obtained for α_2 ($2\,^1P$) between our result and those using the first discrete states [16] may be fortuitous and result from a balance of the positive contributions in the difference of terms $\alpha_2 = \frac{1}{3}(\alpha_{zz} - \alpha_{xx})$.

Figure 1 illustrates the behavior of scalar α_0 polarizability versus electric field pulsations ω up to the second resonance for $2\,^1P$ and $2\,^3P$. Before the first resonance corresponding to the $2P \rightarrow 2S$ transition, α_0 decreases in both cases. Above this resonance, the minimum observed corresponds to the compensation of the decreasing $2S$ contribution and all the other increasing contributions (for the $2\,^1P$ state, the $1\,^1S$ contribution is also negative but becomes important only near the $2\,^1P \rightarrow 1\,^1S$ resonance at high frequencies). The second resonance in fact appears at the singlet and triplet $2P \rightarrow 3S$ transitions expected for $\omega = 0.06393$ and 0.06491 a.u., respectively, and before the $2P \rightarrow 3D$ resonances (see Table I).

Figure 2 represents the variations of α_0 versus imaginary pulsations. Using the procedure described in Sec. II, the numerical calculation of $\sum_i f_{2P\rightarrow i}/6\Delta E_{2P\rightarrow i}$ furnishes 10.2 and 8.54 a.u. for the singlet and triplet states, respectively, even when a direct calculation of $\langle 1s2p_x | \sum_{i,j} x_i x_j + 2z_i z_j | 1s2p_x \rangle / 3$ gives 10.56 and 8.780 a.u., showing that our basis set is nearly complete. Similarly when the dipole moment factor is neglected in our TDGI method, the static α_0 values obtained are about 3-4 % lower, showing that the polynomial contribution obviously becomes weak: it would be null if the basis set were complete [25,26].

The van der Waals C_6 coefficients for the $2\,^1P$-$2\,^1P$, $2\,^3P$-$2\,^3P$ and $2\,^1P$-$2\,^3P$ interactions are all positive, even if the static polarizability of the $2\,^1P$ state of He is negative. For the $2\,^1P$-$2\,^1P$, $2\,^3P$-$2\,^3P$, and $2\,^1P$-$2\,^3P$ interactions, our values are 5.9×10^3, 4.9×10^3, and 5.9×10^3 a.u..

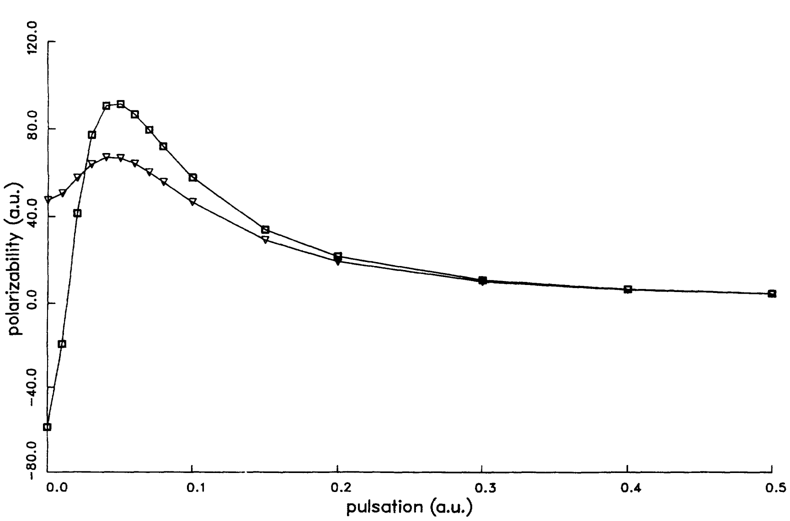

FIG. 2. Dynamic scalar polarizabilities of the singlet (squares) and triplet (triangles) $2P$ states of He versus imaginary pulsations.

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