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Dynamic polarizabilities of rare-earth-metal atoms and dispersion coefficients for their interaction with helium atoms

Xi Chu

Department of Chemistry, University of Montana, Missoula, Montana 59812, USA

Alexander Dalgarno

ITAMP, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA

Gerrit C. Groenenboom

*Theoretical Chemistry, Institute for Molecules and Materials, Radboud University Nijmegen,**Toernooiveld 1, 6525ED, Nijmegen, The Netherlands*

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The dynamic scalar and tensor polarizabilities of the rare-earth-metal atoms are calculated with time-dependent density functional theory. The frequency-dependent polarizabilities at imaginary frequencies are used to determine the isotropic and orientation-dependent van der Waals coefficients for the interactions of the rare-earth-metal atoms with helium atoms. The static polarizabilities are compared with other theoretical values and with experimental results. The agreement is satisfactory in most cases but there are some exceptions where the discrepancy between theory and experiment is significant. The derived isotropic van der Waals coefficients range between 37 and 50 $E_H a_0^6$ and the orientation-dependent coefficients between 2 and $-1 E_H a_0^6$. Thus the ratio of elastic to inelastic scattering cross sections is expected to be substantial and any one of the rare-earth-metal atoms is an excellent candidate for trapping and cooling in a He gas.

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I. INTRODUCTION

Experiments [1] have shown that the cross sections for inelastic momentum transfer in collisions of He atoms with the transition metal atoms scandium and titanium at low temperatures are small, encouraging the belief that Sc and Ti can be trapped and cooled in a He bath gas. The cross sections reflect the anisotropy of the interaction [2,3] which is reduced by the shielding of the inner 5*d* electrons by the outer 4*s* shell [4,5]. A similar reduction has been found for the interaction of thulium with He, arising from the shielding by the outer 6*s* shell [4,5] and large ratios for the elastic to inelastic rates for collisions of He with many of the rare-earth-metal atoms have been determined by experiment [6]. In explicit calculations of inelastic thulium-He collisions a rate coefficient of $1.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at 0.8 K was obtained [7].

At ultracold temperatures the scattering is dominated by the long range van der Waals interaction which varies with the internuclear distance R as $C_6(L, M)/R^6$ where L is the orbital angular momentum quantum number of the open shell atom and M is the projection quantum number, equal to Λ in the body-fixed frame. It is the separations of the different molecular states $|M| \leq L$ that determine the long range anisotropy [8,9]. Promising candidates for trapping and cooling can be identified by calculations of $C_6(L, M)$ [5].

The van der Waals coefficients can be expressed as integrals over the product of the scalar and tensor dynamic polarizabilities of He and the complex atoms, evaluated at imaginary frequencies. We have applied a version of time-dependent density functional theory (TDDFT) [10,11] to the calculation of scalar polarizabilities [12] and the tensor polarizabilities of atoms in P states [13] and of Sc and Ti [14].

We extend it here to include the tensor polarizabilities of the rare-earth-metal atoms. Measurements of the static tensor polarizabilities at zero frequency [15–19] provide a measure of the accuracy of the calculations. The dynamic polarizabilities are then used to determine the orientation-dependent van der Waals coefficients.

II. THEORY

The leading term in the interaction at long range of an open-shell atom with total orbital angular momentum L and projection M with a He atom in a state with $L=0$ in the body-fixed frame is $C_6(L, M)/R^6$. The van der Waals coefficient may be written as [14]

$$C_6(L, M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)} C_{6,2}(L), \quad (1)$$

where $C_{6,0}(L)$ is the isotropic component of the interaction and $C_{6,2}(L)$ is the component corresponding to the $P_2(\cos \theta)$ term in the expansion of the interaction in Legendre polynomials, where the angle θ specifies the orientation in the space-fixed frame [8,9,14].

The dispersion coefficients $C_{6,0}(L)$ and $C_{6,2}(L)$ may be expressed in terms of the scalar and tensor polarizabilities $\alpha_0(L; i\omega)$ and $\alpha_2(L; i\omega)$ evaluated at imaginary frequencies

$$C_{6,0}(L) = \frac{3}{\pi} \int_0^\infty \alpha_0(L; i\omega) \bar{\alpha}_{\text{He}}(i\omega) d\omega \quad (2)$$

and

TABLE I. The scalar and tensor static dipole polarizabilities of rare-earth-metal atoms in D states in units of a_0^3 .

Configuration	Term	α_0	α_2	α_2 [16,17]
Y [Kr] $4d5s^2$	2D	138.97	3.82	3.33
La [Xe] $5d6s^2$	2D	200.86	10.12	10.45
Gd [Xe] $4f^75d6s^2$	9D	160.65	6.27	7.87
Lu [Xe] $4f^{14}5d6s^2$	2D	131.25	5.34	20.98

$$C_{6,2}(L) = -\frac{3(2L+3)}{2\pi L} \int_0^\infty \alpha_2(L; i\omega) \bar{\alpha}_{\text{He}}(i\omega) d\omega, \quad (3)$$

where $\bar{\alpha}_{\text{He}}(\omega)$ is the dynamic polarizability of He. The polarizabilities at imaginary frequencies are given in atomic units by

$$\alpha_{\parallel}(L, M; i\omega) = 2 \sum_{\gamma M_\gamma} \frac{(E_\gamma - E_L) |\langle LM | \hat{z} | L_\gamma M_\gamma \rangle|^2}{(E_\gamma - E_L)^2 + \omega^2}, \quad (4)$$

where E_γ is the energy of the electronically excited state $|L_\gamma M_\gamma\rangle$ and the z axis lies along the internuclear axis. There are $2L+1$ polarizabilities given by

$$\alpha_{\parallel}(L, M) = \alpha_0(L) + \alpha_2(L) \frac{\langle LM20 | LM \rangle}{\langle LL20 | LL \rangle}, \quad (5)$$

where $\alpha_2(L)$ is defined such that for $L=M$, $\alpha_{\parallel}(L, L) = \alpha_0(L) + \alpha_2(L)$.

III. CALCULATION OF POLARIZABILITIES

We calculated $\alpha_{\parallel}(L, L; i\omega)$ and $\alpha_{\parallel}(L, L-1; i\omega)$ of the rare-earth-metal atoms using linear response TDDFT [12–14]. A detailed description of the method is given in Refs. [12,13]. It yields polarizabilities that are exact in the limit of high frequencies, varying as N/ω^2 , where N is the number of electrons in the atom. Our calculated static polarizabilities $\alpha_0(\omega=0)$ and $\alpha_2(\omega=0)$ are presented in Tables I–IV together with other theoretical predictions and with the measured values of $\alpha_2(\omega=0)$.

There have been several calculations of the isotropic static polarizability $\alpha_0(\omega=0)$ of ytterbium, Yb [4,20–23], which has a ground state of S symmetry so that $\alpha_2=0$. Wang, Pan, and Schwarz [20] report a polarizability of $266a_0^3$ from the Hartree-Fock approximation and $132a_0^3$ from a density functional calculation. Wang and Doig [21] and Buchachenko, Szczyński, and Chałasiński [4] used coupled cluster theory. Depending on the details of the method and the size of the

 TABLE II. The scalar and tensor static dipole polarizabilities of rare-earth-metal atoms with total angular momentum $L=3$ in units of a_0^3 .

Configuration	Term	α_0	α_2	α_2 [15,19]
Sm [Xe] $4f^66s^2$	7F	199.96	-4.95	-3.58
Tm [Xe] $4f^{13}6s^2$	2F	161.42	-2.27	-2.73

 TABLE III. The scalar and tensor static dipole polarizabilities of rare-earth-metal atoms with total angular momentum $L=5$ in units of a_0^3 .

Configuration	Term	α_0	α_2	α_2 [19]
Pm [Xe] $4f^56s^2$	6H	206.07	-5.28	
Tb [Xe] $4f^96s^2$	6H	180.94	4.98	4.74
Er [Xe] $4f^{12}6s^2$	3H	165.79	-2.73	-2.85

basis sets, polarizabilities were computed between 88 and $180a_0^3$ with most probable values of $140a_0^3$ [21] and $155a_0^3$ [4]. Porsev, Rakhlina, and Kozlov [22] used a configuration-interaction procedure supplemented by many-body perturbation theory and obtained $\alpha_0=118a_0^3$ with a possible uncertainty of $45a_0^3$. Porsev and Derevianko [23] used relativistic many-body perturbation theory to get a value of $111.3a_0^3$ with a claimed uncertainty of $0.5a_0^3$. Our TDDFT procedure yields $\alpha_0=157a_0^3$ in close agreement with Ref. [4]. The high accuracy 0.5% claimed by Porsev and Derevianko is derived from their assumption that over 95% of the polarizability comes from the transition in the summation in Eq. (4) connecting the ground S state to the lowest excited P state, the matrix element of which has been determined to high precision by Takasu *et al.* [24]. We have in progress elaborate calculations of $\alpha_0(\omega=0)$ in order to resolve the discrepancies.

The experimental data on α_2 usually refers to measured values for the individual fine-structure states $^{2S+1}L_J$. To an excellent approximation, they can be reduced to a single value $\alpha_2(L)$ by using the relationship [25,26]

$$\alpha_2(^{2S+1}L_J) = (-1)^{S+L+J} (2J+1) \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix} \begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix} \times \begin{pmatrix} L & 2 & L \\ -L & 0 & L \end{pmatrix}^{-1} \alpha_2(L). \quad (6)$$

The experimental values of $\alpha_2(L)$ in the tables were obtained using this equation when only $\alpha_2(^{2S+1}L_J)$ was reported. When $\alpha_2(^{2S+1}L_J)$ was reported for several values of J , $\alpha_2(L)$ was obtained from a linear least squares fit using this equation.

Table I compares the measured static tensor polarizabilities of rare-earth-metal atoms in ground 2D states [16,17] with the TDDFT values. Because the determination of α_2 involves the subtraction of two large quantities, the agree-

 TABLE IV. The scalar and tensor static dipole polarizabilities of rare-earth-metal atoms with total angular momentum $L=6$ in units of a_0^3 .

Configuration	Term	α_0	α_2	α_2 [19]
Pr [Xe] $4f^36s^2$	4I	220.07	6.13	1.81
Nd [Xe] $4f^46s^2$	5I	212.72	-5.63	-1.69
Dy [Xe] $4f^{10}6s^2$	5I	175.46	-4.50	1.41
Ho [Xe] $4f^{11}6s^2$	4I	170.45	-3.19	-1.17

ment between theory and measurement can be regarded as satisfactory with the exception of lutetium, Lu, for which there is a discrepancy by a factor of 4. The values of α_2 are controlled largely by the $5d$ electron. It appears that screening by the $4f$ electrons is less effective in Gd than in Lu, leading to an increase in the binding energy of the $5d$ electrons and a decrease in the polarizabilities. In contrast the screening is more effective in Lu, leading to a decrease in the binding energy and an increase in α_2 [17] and likely also in α_0 . TDDFT does not reproduce this behavior and the resulting value of α_0 may be too small.

In Table II a similar comparison is made for the ground F states of samarium and thulium. The agreement is good both in magnitude and in sign, α_2 being negative for both Sm and Tm. For Tm, α_0 has been calculated by Buchachenko *et al.* [4] who obtained values in the range $(89-152)a_0^3$, with the upper limit as the most likely, in comparison to our result $\alpha_0=161a_0^3$. For α_2 , Buchachenko *et al.* calculated values between -1.5 and $-2.1a_0^3$ whereas we found $-2.27a_0^3$. The experiments [18,19] yielded $-2.73a_0^3$.

Table III lists the results for the $L=5$ ground H states of promethium, terbium, and erbium. The experiments to determine α_2 for Tb and Er were carried out by Rinkleff and Thorn [19]. Theory and experiment agree closely.

Table IV reports the measured [19] and the predicted tensor polarizabilities for the $L=6$ I states of praseodymium, neodymium, dysprosium, and holmium. There are differences of about a factor of 4 and for Dy even the sign is incorrect. The calculation involves the small difference of two large quantities $\alpha(6,6)$ and $\alpha(6,5)$ and it is difficult to achieve numerical convergence for states with high values of M .

IV. CALCULATION OF THE VAN DER WAALS COEFFICIENTS

Equations (2) and (3) were used to evaluate $C_{6,0}$ and $C_{6,2}$ for the interactions of the rare-earth-metal atoms with He. The frequency-dependent dipole polarizability of He is available from high precision variational calculations of Jamieson *et al.* [27]. Van der Waals coefficients were calculated previously for He interacting with Tm [4,7,28] and Yb [4,28].

Our results for the static dipole polarizabilities of the rare-earth-metal atoms and the corresponding values of $C_{6,0}$ and $C_{6,2}$ for their interactions with He are listed in Table V. For $C_{6,0}$ of Yb-He we obtain $39.4E_H a_0^6$ in good agreement with the values of 45.0 and $44.5E_H a_0^6$ of Buchachenko *et al.* [4,28], where E_H is the Hartree unit of energy. Buchachenko *et al.* [4,28] also carried out sophisticated calculations for Tm-He obtaining $C_{6,0}=41.2E_H a_0^6$ and $C_{6,2}=0.10E_H a_0^6$ and more recently [28] $C_{6,0}=41.8E_H a_0^6$ and $C_{6,2}=0.14E_H a_0^6$. We obtain $C_{6,0}=40.1E_H a_0^6$ and $C_{6,2}=0.50E_H a_0^6$, in remarkably close agreement. In Table 1 of Ref. [28] our preliminary values for these last two numbers were reported. These values were slightly lower because less accurate dynamic polarizabilities of He were used.

We also computed the dispersion coefficients for TmYb and Yb₂. For TmYb we obtain $C_{6,0}=2338.9E_H a_0^6$ and $C_{6,2}=39.6E_H a_0^6$, in good agreement with the *ab initio* values of

TABLE V. The scalar and tensor static dipole polarizabilities (in units of a_0^3) and isotropic and anisotropic dispersion coefficients (in units of $E_H a_0^6$).

	Configuration	Term	α_0	α_2	$C_{6,0}$	$C_{6,2}$
Y	[Kr] $4d5s^2$	2D	138.97	3.82	38.19	-0.96
La	[Xe] $5d6s^2$	2D	200.86	10.12	49.26	-1.89
Ce ^a	[Xe] $4f5d6s^2$	3H	193.51	8.54	48.06	-1.70
Pr	[Xe] $4f^36s^2$	4I	220.07	6.13	48.84	-1.22
Nd	[Xe] $4f^46s^2$	5I	212.72	-5.63	47.78	1.07
Pm	[Xe] $4f^56s^2$	6H	206.07	-5.28	46.80	0.97
Sm	[Xe] $4f^66s^2$	7F	199.96	-4.95	45.88	1.08
Eu	[Xe] $4f^76s^2$	8S	194.27	0.0	45.01	0.0
Gd	[Xe] $4f^75d6s^2$	9D	160.65	6.27	42.52	-1.72
Tb	[Xe] $4f^96s^2$	6H	180.94	4.98	43.12	-1.10
Dy	[Xe] $4f^{10}6s^2$	5I	175.46	-4.50	42.30	0.83
Ho	[Xe] $4f^{11}6s^2$	4I	170.45	-3.19	41.53	0.59
Er	[Xe] $4f^{12}6s^2$	3H	165.79	-2.73	40.80	0.52
Tm	[Xe] $4f^{13}6s^2$	2F	161.42	-2.27	40.10	0.50
Yb	[Xe] $4f^{14}6s^2$	1S	157.30	0.0	39.44	0.0
Lu	[Xe] $4f^{14}5d6s^2$	2D	131.25	5.34	37.62	-1.38

^aThe 1G ground state of Ce has a leading 29% admixture of the 3H term. Since our DFT based method requires a single determinant representation of the state, we cannot calculate the 1G term and we report the results for the high-spin 3H term.

2172.6 and $14.6E_H a_0^6$, respectively [28]. For Yb₂ we compute $C_{6,0}=2291.6E_H a_0^6$, again in good agreement with the value of $2567.9E_H a_0^6$ of Ref. [28].

Note that if atoms with a partly filled d shell in Table V are ignored, there is a steady decrease of both α_0 and $C_{6,0}$ with increasing atomic number. The atoms with partly filled d shells have relatively low polarizabilities.

The values of $C_{6,0}$ reported in Table V vary little from one rare-earth-metal atom to another, all lying between 37 and $50E_H a_0^6$, suggesting that they arise largely from the excitation of the outer $6s$ shells. The magnitudes are such that the momentum transfer cross sections that control the cooling of the rare-earths-metal atoms in a gas of He are likely to be substantial. In contrast, the values of $C_{6,2}$ are all small, varying from -1.89 to $1.08E_H a_0^6$. Although there are some uncertainties in the values of the tensor polarizabilities of Lu, Pr, Nd, and Ho, they do not change the conclusion that due to the screening effect of the outer $6s$ shell the inelastic collisions that lead to trap loss will be inefficient. Any one of the rare-earths-metal atoms is a promising candidate for trapping and cooling in a He bath gas.

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