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Polarizabilities of Sc and Ti atoms and dispersion coefficients for their interaction with helium atoms

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The dynamic scalar and tensor polarizabilities of Sc and Ti are computed with time-dependent density functional theory. These polarizabilities are used to compute the isotropic and anisotropic dispersion interactions in ScHe and TiHe. We find $C_{6,0}(\text{ScHe})=30.00$, $C_{6,2}(\text{ScHe})=-1.63$, $C_{6,0}(\text{TiHe})=28.40$, and $C_{6,2}(\text{TiHe})=-0.90$ ($E_h a_0^6$). We show that an estimate of the dispersion anisotropy based on static polarizabilities results in an overestimation by a factor of 2.

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I. INTRODUCTION

Experiments [1] have demonstrated that the cross sections for angular momentum transfer in collisions of ^3He atoms with rare earth gas atoms are small so that rare earth gas atoms can be cooled and trapped in a helium buffer gas. The ratio of the elastic and inelastic cross sections for Sc($3d4s^2\ ^2D$) and Ti($3d^24s^2\ ^3F$) atoms have been measured and are large [2]. The inelastic cross sections are controlled by the differences between the potential energy curves of the molecular symmetries populated by the approach of the complex atoms and helium [3,4]. The differences are small due to the shielding effects of the outermost shell of $4s$ electrons which diminish the anisotropy of the interactions between Sc and Ti and ^3He , as made evident by refined quantum chemistry calculations [4,5]. The calculations were carried out at intermediate and short internuclear distances. They lose accuracy at large distances where the interaction is the long range van der Waals interaction to which the cross sections are sensitive. Calculations of the van der Waals or dispersion coefficients for the interactions of complex atoms can be carried out to high precision [6,7] and in themselves provide an assessment of the likelihood that specific atoms can be cooled in magnetic traps. We present detailed estimates of the leading dispersion coefficients for the individual symmetry states of the molecules ScHe and TiHe.

II. THEORY

The second order interaction between an open-shell atom with total orbital angular momentum L and a S -state atom such as helium can be represented by an effective interaction potential $\hat{V}$ acting in the $2L+1$ dimensional space $\{|LM\rangle, M=-L, \dots, L\}$, where M is the projection of the angular momentum on the internuclear axis. The effective interaction potential $\hat{V}(R, \theta)$ is a function of the internuclear distance R and the angle θ that specifies the orientation of the non-spherical atom with respect to the internuclear axis [8–12]. We expand $\hat{V}$ in Legendre polynomials $P_K(\cos \theta)$,

$$\hat{V}(R, \theta) = \sum_K v_K(R) P_K(\cos \theta), \quad (1)$$

where R is the internuclear distance and θ is the polar angle of the effective electron. The molecular potentials $V_M(R)$ are related to the effective potential through

$$V_M(R) = \langle LM | \hat{V} | LM \rangle = \sum_K v_K(R) \langle LMK0 | LM \rangle \langle L0K0 | L0 \rangle. \quad (2)$$

The potentials V_M are only labeled by M because this is a good molecular quantum number; $M=0, 1, 2$, and 3 corresponds to Σ, Π, Δ , and Φ molecular states. The expansion coefficients v_K can be obtained from the molecular potentials by inverting this equation [9],

$$v_K(R) = \frac{[K]}{[L]} \sum_{M=-L}^L \frac{\langle LMK0 | LM \rangle}{\langle L0K0 | L0 \rangle} V_M(R), \quad (3)$$

where we used the orthogonality relation of Clebsch-Gordan coefficients,

$$\sum_{M=-L}^L \langle LMK0 | LM \rangle^2 = \frac{[L]}{[K]} \quad (4)$$

and $[X]=2X+1$. At large distances R the leading term in the potential is the dispersion interaction

$$V_M(R) \simeq - \frac{C_6(L, M)}{R^6}. \quad (5)$$

The C_6 coefficients may be calculated as [13]

$$C_6(L, M) = \frac{2}{\pi} \int_0^\infty \alpha_{zz}(L, M; i\omega) \bar{\alpha}_{\text{He}}(i\omega) d\omega + \frac{1}{\pi} \int_0^\infty \alpha_{xx}(L, M; i\omega) \bar{\alpha}_{\text{He}}(i\omega) d\omega. \quad (6)$$

The dynamic dipole-dipole polarizabilities at imaginary fre-

quency $i\omega$ of state $|LM\rangle$ with energy E_L , $\alpha_{uu}(L, M; i\omega)$, for $u \in \{x, y, z\}$, in atomic units, are given by

$$\alpha_{uu}(L, M; i\omega) = 2 \sum_{\gamma M_\gamma} \frac{(E_\gamma - E_L) |\langle LM | \hat{\mu}_u | \gamma L_\gamma M_\gamma \rangle|^2}{(E_\gamma - E_L)^2 + \omega^2}, \quad (7)$$

where $\hat{\mu}_u$ are the Cartesian components of the electric dipole operator and E_γ is the energy of the excited electronic state $|\gamma L_\gamma M_\gamma\rangle$. For $u=z$ the summation involves only $M_\gamma=M$ and for $u=x$ we have $M_\gamma=M\pm 1$. The z component refers to the internuclear axis so we define $\alpha_{||}=\alpha_{zz}$ and $\alpha_{\perp}=\alpha_{xx}=\alpha_{yy}$. The $2(2L+1)$ polarizabilities can be expressed in terms of the scalar polarizability $\alpha_0(L; i\omega)$ and the tensor polarizability [14,15] $\alpha_2(L; i\omega)$ (dropping the ω dependence for compactness),

$$\begin{aligned} \alpha_{||}(L, M) &= \alpha_0(L) + \alpha_2(L) \frac{\langle LM20 | LM \rangle}{\langle LL20 | LL \rangle} \\ &= \alpha_0(L) + \alpha_2(L) \frac{3M^2 - L(L+1)}{L(2L-1)}, \end{aligned} \quad (8)$$

$$\alpha_{\perp}(L, M) = \alpha_0(L) - \frac{1}{2} \alpha_2(L) \frac{3M^2 - L(L+1)}{L(2L-1)}, \quad (9)$$

where the tensor polarizability is defined such that for $L=M$, $\alpha_{||}(L, L) = \alpha_0(L) + \alpha_2(L)$. For completeness we derive these expressions in the Appendix, where we also give the relation between the spherical and Cartesian components of the polarizabilities. From Eqs. (8) and (9) we see that all polarizabilities can be found if the parallel and perpendicular components of the polarizability for a single $|LM\rangle$ state are known,

$$\bar{\alpha}(L) \equiv \frac{1}{3} \alpha_{||}(L, M) + \frac{2}{3} \alpha_{\perp}(L, M) = \alpha_0(L), \quad (10)$$

$$\Delta\alpha(L, M) \equiv \alpha_{||}(L, M) - \alpha_{\perp}(L, M) = \frac{3}{2} \alpha_2(L) \frac{3M^2 - L(L+1)}{L(2L-1)}. \quad (11)$$

Alternatively, we may use Eq. (4) to derive

$$\alpha_K(L) = \frac{[K]}{[L]} \langle LLK0 | LL \rangle \sum_{M=-L}^L \langle LMK0 | LM \rangle \alpha_{||}(L, M) \quad (12)$$

or, explicitly

$$\alpha_0(L) = [L]^{-1} \sum_{M=-L}^L \alpha_{||}(L, M), \quad (13)$$

$$\begin{aligned} \alpha_2(L) &= \frac{5}{(L+1)(2L+1)(2L+3)} \\ &\times \sum_{M=-L}^L [3M^2 - L(L+1)] \alpha_{||}(L, M). \end{aligned} \quad (14)$$

Equation (13) also holds when we replace $\alpha_{||}$ by $\alpha_{\perp}$ and in Eq. (14) we may replace $\alpha_{||}$ by $-2\alpha_{\perp}$ [see Eqs. (8) and (9)]. From Eq. (13) the scalar polarizabilities for P , D , and F state atoms are

$$\alpha_0(P) = [\alpha_{||}(1, 0) + 2\alpha_{||}(1, 1)]/3,$$

$$\alpha_0(D) = [\alpha_{||}(2, 0) + 2\alpha_{||}(2, 1) + 2\alpha_{||}(2, 2)]/5,$$

$$\alpha_0(F) = [\alpha_{||}(3, 0) + 2\alpha_{||}(3, 1) + 2\alpha_{||}(3, 2) + 2\alpha_{||}(3, 3)]/7 \quad (15)$$

and from Eq. (14) we find the tensor polarizabilities,

$$\alpha_2(P) = [\alpha_{||}(1, 1) - \alpha_{||}(1, 0)]/3,$$

$$\alpha_2(D) = [-2\alpha_{||}(2, 0) - 2\alpha_{||}(2, 1) + 4\alpha_{||}(2, 2)]/7,$$

$$\alpha_2(F) = [-10\alpha_{||}(3, 0) - 15\alpha_{||}(3, 1) + 25\alpha_{||}(3, 3)]/42. \quad (16)$$

In analogy to Eq. (3) we define the scalar ($K=0$) and tensor ($K>0$) components of the dispersion coefficients

$$C_{6,K}(L) = \frac{[K]}{[L]} \sum_{M=-L}^L \frac{\langle LMK0 | LM \rangle}{\langle L0K0 | L0 \rangle} C_6(L, M). \quad (17)$$

Substituting Eqs. (6), (8), and (9) into Eq. (17) shows that $C_{6,0}(L)$ depends on $\alpha_0(L; i\omega)$,

$$C_{6,0}(L) = \frac{3}{\pi} \int_0^\infty \alpha_0(L; i\omega) \bar{\alpha}_{\text{He}}(i\omega) d\omega \quad (18)$$

and that $C_{6,2}(L)$ depends on $\alpha_2(L; i\omega)$

$$C_{6,2}(L) = -\frac{3(2L+3)}{2\pi L} \int_0^\infty \alpha_2(L; i\omega) \bar{\alpha}_{\text{He}}(i\omega) d\omega \quad (19)$$

and all other $C_{6,K}$ coefficients should be zero. Hence we can invert Eq. (17) [or use Eq. (2)] to express all dispersion coefficients as

$$C_6(L, M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)} C_{6,2}(L). \quad (20)$$

If the ratio $\alpha_2(i\omega)/\alpha_0(i\omega)$ is assumed to be independent of ω then we can estimate the anisotropy from the ratio of Eqs. (18) and (19)

$$\frac{C_{6,2}(L)}{C_{6,0}(L)} \approx -\frac{2L+3}{2L} \frac{\alpha_2(L)}{\alpha_0(L)}. \quad (21)$$

III. COMPUTATIONAL METHOD

The dynamic polarizabilities $\alpha_{||,\perp}(L, M; i\omega)$ of Sc and Ti were computed using a linear response time-dependent density functional theory (TDDFT). A detailed description of the method is given in Refs. [6,7]. The TDDFT method has with few exceptions yielded polarizabilities good to within an uncertainty of about 5%. The TDDFT polarizabilities are exact in the limit of high frequencies, varying asymptotically as N/ω^2 , where N is the number of electrons in the system [6].

The DFT based approach applies to cases where a single determinant can be found as a reference to describe the

TABLE I. The scalar and tensor static dipole polarizabilities of Sc and Ti (in a_0^3).

	Sc		Ti	
	α_0	α_2	α_0	α_2
This paper	105.88	6.31	94.69	3.97
Ref. [17]	150.57	5.36	129.34	2.17
Ref. [18]	107		91.4	
Ref. [20] ^a	123.60	5.38	104.05	2.06
Ref. [20] ^b	121.22	5.24	101.57	2.01

^aNonrelativistic.

^bWith Douglas-Kroll relativistic corrections.

atomic state. For Sc($3d4s^2\ ^2D$) we can compute all six polarizabilities ($|M|=0,1,2, \parallel, \perp$) but for Ti($3d^24s^2\ ^3F$) only $M=2$ and $M=3$ are qualified and we compute four polarizabilities. Theoretically we can obtain the scalar and tensor polarizabilities, and hence all others, by solving the linear Eqs. (8) and/or (9) using only two independent polarizabilities $\alpha_{\parallel,\perp}(L,M;i\omega)$. Instead we use a linear least squares fit to obtain the best possible $\alpha_0(L)$ and $\alpha_2(L)$ and we use the deviations from Eqs. (8) and/or (9) to check the internal consistency of the method and to obtain an error estimate.

The dynamic polarizability of helium has been determined to high precision by a large scale variational calculation [16]. We use it together with the scalar and tensor polarizabilities obtained from the least squares fit to the TDDFT results to compute the dispersion coefficients $C_{6,0}(L)$ [Eq. (18)] and $C_{6,2}(L)$ [Eq. (19)].

IV. RESULTS AND DISCUSSION

In Table I we present the scalar and tensor static polarizabilities of Sc and Ti obtained from the least squares fits. The results for Ti were obtained from a fit to $\alpha_{\parallel}(3,2)=94.78$, $\alpha_{\parallel}(3,3)=98.62$, $\alpha_{\perp}(3,2)=94.78$, and $\alpha_{\perp}(3,3)=92.63a_0^3$. The six static polarizabilities [$\alpha_{\parallel,\perp}(L,M)$] computed for Sc are shown in Fig. 1. This figure also shows that the results for Sc are represented quite well by the scalar and tensor polarizabilities

FIG. 1. The static polarizabilities $\alpha_{\parallel}(LM)$ (the circles) and $\alpha_{\perp}(LM)$ (the crosses) of Sc for $M=0, 1$, and 2 . The solid lines represent the result of a linear least squares fit using Eqs. (8) and (9).

FIG. 2. The dynamic polarizabilities of Sc and Ti at imaginary frequencies. Plot (a) shows the scalar polarizabilities $\alpha_0(i\omega)$ for Sc and Ti. Plot (b) shows the tensor polarizabilities $\alpha_2(i\omega)$ for Sc (solid line) and Ti (dashed line) and also the relative tensor polarizabilities $\alpha_2(i\omega)/\alpha_0(i\omega)$ [multiplied with $\alpha_0(0)$ to make it coincide with $\alpha_2(i\omega)$ for $\omega=0$] for Sc (dotted-dashed line) and for Ti (dotted line).

abilities $\alpha_0(2)$ and $\alpha_2(2)$; the root-mean-square deviation is 0.3%, which in an exact theory would be zero. If we were to compute $\alpha_2(2)$ from $\alpha_{\parallel}(2,2)$ and $\alpha_{\perp}(2,2)$ according to Eq. (11) this 0.3% error would introduce an uncertainty in $\alpha_2(2)$ of up to 7%.

In Table I we compare our static polarizabilities with the results of variational configuration interaction calculations by Stiehler and Hinze [17]. They remark that their values are probably too large. Our scalar polarizabilities are indeed smaller, and in better agreement with the variational perturbation calculations of Chandler and Glass [18] and recent calculations by Kłos [5]. The only theoretical tensor polarizabilities that we found are those that can be derived from the $\alpha_{\parallel}(L,M)$ of Stiehler and Hinze. These agree in sign but they are smaller than ours by 15% and 45% for Sc and Ti, respectively. Our value of 6.31 for α_2 for Sc is consistent with the experimental value of 6.0(4) of Rinkleff and Thorn [19].

Figure 2 presents the scalar and tensor dynamic polarizabilities of Sc and Ti as a function of the imaginary frequency. At each frequency the polarizabilities were obtained from a linear least squares fit. Sometimes the anisotropy in dispersion coefficients is estimated from the relative anisotropy in the static polarizability [$\alpha_2(L)/\alpha_0(L)$, see Eq. (21)] [20,21]. Therefore we also show in plot (b) how the relative anisotropy depends on the imaginary frequency. The relative anisotropy for $\omega>0$ is always smaller than for $\omega=0$. For high frequencies it goes to zero, which is expected because both $\alpha_{zz}(i\omega)$ and $\alpha_{xx}(i\omega)$ vary as N/ω^2 asymptotically.

In Table II we present the dispersion coefficients. The first four entries are the dispersion coefficients computed from the parallel and perpendicular polarizabilities using Eq. (6). From these results we computed the isotropic and anisotropic dispersion coefficients for Sc using Eq. (17) and for Ti by solving two linear equations [Eq. (20), with $M=2, 3$] for $C_{6,0}$ and $C_{6,2}$. We also computed the isotropic and anisotropic dispersion coefficients directly from the isotropic and aniso-

TABLE II. Dispersion coefficients for He-Sc and He-Ti (in $E_h a_0^6$). We consider the results obtained from Eqs. (18) and (19) to be our most accurate.

		Sc	Ti
$C_6(\Sigma)$	Eq. (6)	29.56	
$C_6(\Pi)$	Eq. (6)	29.74	
$C_6(\Delta)$	Eq. (6)	30.50	28.40
$C_6(\Phi)$	Eq. (6)		28.68
$C_{6,0}$	Eqs. (17) and (20)	30.01	28.40
$C_{6,0}$	Eq. (18)	30.00	28.39
$C_{6,0}$	Ref. [5]	31.4	25
$C_{6,2}$	Eqs. (17) and (20)	-1.71	-0.84
$C_{6,2}$	Eq. (19)	-1.63	-0.89
$C_{6,2}$	Eq. (21)	-3.13	-1.78
$C_{6,2}$	Ref. [5]	-0.14	
$C_{6,2}$	Ref. [20] ^a	-2.39	
$C_{6,2}$	Ref. [20] ^b	-1.51	

^aEstimate based on the relative anisotropy in the static polarizability.

^bFrom a fit to MRCI potentials.

tropic polarizabilities shown in Fig. 2 using Eqs. (18) and (19). The results are very similar. We prefer the method using Eqs. (18) and (19) since it employs scalar and tensor polarizabilities obtained from a linear least squares fit to all computed polarizabilities, which possibly reduces numerical “noise.”

Dispersion coefficients for ScHe and TiHe have been derived by Klos *et al.* [5,20] by fitting *ab initio* potential energy curves and they are included in the table. For the isotropic dispersion interaction in ScHe the results agree within 5% and for TiHe the difference is 12%. Klos *et al.* remark that the accuracy of their long-range potentials for TiHe was not sufficient to extract isotropic and anisotropic C_6 coefficients

and their result is an estimate. Klos *et al.* also give an estimate of $C_{6,2}$ for ScHe based on the relative anisotropy in the static polarizability which is more than an order of magnitude larger than the result of the fit [5]. When we follow the same procedure [i.e., using Eq. (21)] we find that this overestimates the anisotropy by a factor of 2 for ScHe as well as TiHe (see Table II). This overestimate can be understood from the frequency dependence of the relative anisotropy shown in Fig. 2.

V. CONCLUSION

We have presented isotropic and anisotropic dispersion coefficients for ScHe and TiHe. The coefficients were computed employing dynamic polarizabilities computed with a TDDFT method. The redundancy in the open-shell atomic polarizabilities is used to check the internal consistency of the method and to enhance the accuracy of the computed polarizabilities. We show that a determination of the dispersion anisotropy based on static polarizabilities results in an overestimation by a factor of 2.

Our calculations confirm earlier estimates that the anisotropy in the long range interaction is small, which suggests that the inelastic rates and trap loss of Sc and Ti in a buffer gas cooling experiment will be slow.

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APPENDIX: DERIVATION OF EQS. (8) AND (9)

The spherical components of the dynamic dipole-dipole polarizability are defined by

$$\alpha_{q,-q}(L,M;i\omega) = \sum_{\gamma M_\gamma} (E_\gamma - E_0) \frac{[\langle LM|\hat{\mu}_q|\gamma L_\gamma M_\gamma\rangle\langle\gamma L_\gamma M_\gamma|\hat{\mu}_{-q}|LM\rangle + \langle LM|\hat{\mu}_{-q}|\gamma L_\gamma M_\gamma\rangle\langle\gamma L_\gamma M_\gamma|\hat{\mu}_q|LM\rangle]}{(E_\gamma - E_0)^2 + \omega^2}, \quad (\text{A1})$$

where the spherical components of the dipole operator are defined by $\hat{\mu}_0 = \hat{\mu}_z$ and $\hat{\mu}_\pm = \mp 2^{-1/2}(\hat{\mu}_x \pm i\hat{\mu}_y)$. The dipole operator can be expressed in unit spherical tensor operators of rank one [22]

$$\hat{\mu}_q = \frac{1}{\sqrt{3}} \sum_{\gamma_1 L_1 \gamma_2 L_2} \hat{T}_{1,q}(\gamma_1 L_1; \gamma_2 L_2) \langle \gamma_1 L_1 \| \hat{\mu} \| \gamma_2 L_2 \rangle, \quad (\text{A2})$$

where

$$\hat{T}_{kq}(\gamma_1 j_1; \gamma_2 j_2) = \sum_{m_1 m_2} |\gamma_1 j_1 m_1\rangle \langle \gamma_2 j_2 m_2| \times (-1)^{j_1 - m_1} [k]^{1/2} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \quad (\text{A3})$$

and $\langle \gamma_1 L_1 \| \hat{\mu} \| \gamma_2 L_2 \rangle$ is the reduced matrix element from the Wigner-Eckart theorem. For the spherical tensor operators we have the general relation

$$\begin{aligned} & \hat{T}_{k_1 q_1}(\gamma_1 j_1; \gamma_2 j_2) \hat{T}_{k_2 q_2}(\gamma_2 j_2; \gamma_3 j_3) \\ &= \sum_{KQ} \hat{T}_{KQ}(\gamma_1 j_1; \gamma_3 j_3) [k_1]^{1/2} [k_2]^{1/2} (-1)^{j_1+j_3+K} \\ & \times \begin{Bmatrix} j_1 & j_2 & k_1 \\ k_2 & K & j_3 \end{Bmatrix} \langle k_1 q_1 k_2 q_2 | KQ \rangle. \end{aligned} \quad (\text{A4})$$

Substituting Eqs. (A2)–(A4) into Eq. (A1) we derive

$$\begin{aligned} \alpha_{q,-q}(L, M; i\omega) &= \alpha_0(L; i\omega) \frac{\langle 1q1 - q | 00 \rangle}{\langle 1010 | 00 \rangle} \\ &+ \alpha_2(L; i\omega) \frac{\langle LM20 | LM \rangle \langle 1q1 - q | 20 \rangle}{\langle LL20 | LL \rangle \langle 1010 | 20 \rangle}, \end{aligned} \quad (\text{A5})$$

where

$$\begin{aligned} \alpha_K(L; i\omega) &= \frac{2[K]^{1/2}}{[L]^{1/2}} \sum_{\gamma} \frac{(E_{\gamma} - E_0) |\langle L || \hat{\mu} || \gamma L_{\gamma} \rangle|^2}{(E_{\gamma} - E_0)^2 + \omega^2} \\ &\times (-1)^{L+L_{\gamma}} \begin{Bmatrix} L & L_{\gamma} & 1 \\ 1 & K & L \end{Bmatrix} \langle 1010 | K0 \rangle \langle LLK0 | LL \rangle. \end{aligned} \quad (\text{A6})$$

For $\omega=0$ this expression corresponds to Eq. (19) in Ref. [15] and Eqs. (3.20) and (3.21) in Ref. [14] [remember that $\langle L || \hat{\mu} || \gamma L_{\gamma} \rangle = (-1)^{L-L_{\gamma}} \langle \gamma L_{\gamma} || \hat{\mu} || L \rangle^*$]. Using $\hat{\mu}_{-q}^{\dagger} = (-1)^q \hat{\mu}_q$ one readily derives

$$\alpha_{0,0}(L, M; i\omega) = \alpha_{||}(L, M; i\omega), \quad (\text{A7})$$

$$\alpha_{1,-1}(L, M; i\omega) = -\alpha_{\perp}(L, M; i\omega), \quad (\text{A8})$$

and by substituting explicit expressions for the Clebsch-Gordan coefficients we can derive Eqs. (8) and (9) from Eq. (A5).

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