Coupled cluster response calculations of two-photon transition probability rate constants for helium, neon and argon

Christof Hättig, Ove Christiansen, and Poul Jørgensen
Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

(Received 12 November 1997; accepted 19 February 1998)

The implementation of two-photon transition moments is described for the hierachy of coupled cluster models CCS, CC2 and CCSD and applications are reported for the two-photon transition probability rate constants for transitions from the ground state to the first excited $^1S^e$ state in helium and to the lowest $^1D^e$ and $^1S^e$ states in neon and argon. At the CCSD level the rate constant for the $^1D^e$ transition in argon is in good agreement with the experimental rate constant and also with a recent MCSCF calculation. © *1998 American Institute of Physics.* [S0021-9606(98)02620-8]

I. INTRODUCTION

The two-photon transition probability rate is in lowest order of perturbation theory determined by the two-photon transition moments.[1] In the previous article[2] we have derived general expressions for multiphoton transition moments for coupled cluster methods from the residues of quadratic and higher response functions and, alternatively, as derivatives of transition moment functionals. One of the major advantages of the latter approach is that the Lagrangian technique[3,4] can be used to derive computational efficient expressions, where only a minimal number of response equations need to be solved.

Two-photon transition moments have been calculated previously using the random phase approximation (RPA) and an equation-of-motion technique.[5] Recently Hettema *et al.*[6] have reported an implementation of two-photon transition moments for multiconfiguration self-consistent field (MCSCF) wave functions. High-order response properties are sensitive to the treatment of dynamical electron correlation, which efficiently can be considered using Møller-Plesset perturbation theory or coupled cluster theory. However, only iterative approaches as in the coupled cluster hierachy CCS, CC2,[7] CCSD, CC3[8,9] and CCSDT provide an improved pole structure and can therefore give frequency-dependent properties with a systematic improvement of both the correlation treatment and the pole structure. A systematic improvement of the poles cannot be obtained in Møller-Plesset perturbation theory, where the pole structure is determined by RPA excitation energies and SCF orbital energy differences.

In the present article we report the implementation of two-photon transition moments for the hierachy of coupled cluster models CCS, CC2 and CCSD based on the derivations in Ref. 2 and present calculations of the two-photon transition probability rate constants from the ground state to the lowest one-photon dipole-forbidden but two-photon allowed transitions in helium, neon and argon.

II. TWO-PHOTON TRANSITION MOMENTS FOR THE COUPLED CLUSTER MODELS CCS, CC2 AND CCSD

For exact states the expression for the two-photon transition moment between the ground state $|0\rangle$ and an excited state $|f\rangle$ in the dipole approximation is given as:[1,2,10]

$$M^{\alpha\beta}_{f\leftarrow 0}(\omega_\beta)=\sum_{n\neq 0}\left[\frac{\langle f|(\beta-\langle 0|\beta|0\rangle)|n\rangle\langle n|\alpha|0\rangle}{\omega_\alpha-\omega_{n0}}+\frac{\langle f|(\alpha-\langle 0|\alpha|0\rangle)|n\rangle\langle n|\beta|0\rangle}{\omega_\beta-\omega_{n0}}\right] \tag{1}$$

$$=\hat{P}^{\alpha\beta}(\omega_\alpha,\omega_\beta)\sum_n\frac{\langle f|\beta|n\rangle\langle n|\alpha|0\rangle}{\omega_\alpha-\omega_{n0}}. \tag{2}$$

In Eq. (1) α and β are components of the dipole operator ($\alpha,\beta=x,y,z$), ω_{n0} is the excitation energy from the ground state to state $|n\rangle$, and ω_α and ω_β are the photon energies which satisfy the matching condition $\omega_\alpha+\omega_\beta=\omega_{f0}$. The operator $\hat{P}^{\alpha\beta}(\omega_\alpha,\omega_\beta)$ symmetrizes with respect to permutation of α and β together with their associated frequencies ω_α and ω_β. The two-photon transition moments are symmetric under permutation of the operators α and β if at the same time the frequency argument ω_β is exchanged by $\omega_{f0}-\omega_\beta$:

$$M^{\alpha\beta}_{f\leftarrow 0}(\omega_\beta)=M^{\beta\alpha}_{f\leftarrow 0}(\omega_{f0}-\omega_\beta). \tag{3}$$

In exact state response theory or for variational *ab initio* methods with a orthonormal parametrization for bra and ket states, the two-photon transition moments are in addition symmetric with respect to complex conjuation and a simultaneous inversion of the signs of the frequencies and exchange of the initial and final states:

$$M^{\alpha\beta}_{f\leftarrow 0}(\omega_\beta)=\sum_n\left[\frac{\langle f|\beta|n\rangle\ \langle n|\alpha|0\rangle}{\omega_\alpha-\omega_{n0}}+\frac{\langle f|\alpha|n\rangle\ \langle n|\beta|0\rangle}{\omega_\beta-\omega_{n0}}\right]$$

$$=\sum_n\left[\frac{\langle 0|\alpha|n\rangle^*\langle n|\beta|f\rangle^*}{(\omega_{f0}-\omega_\beta)-\omega_{n0}}+\frac{\langle 0|\beta|n\rangle^*\langle n|\alpha|f\rangle^*}{(\omega_{f0}-\omega_\alpha)-\omega_{n0}}\right]$$

$$=\sum_n\left[\frac{\langle 0|\alpha|n\rangle\ \langle n|\beta|f\rangle}{-\omega_\beta-\omega_{nf}}+\frac{\langle 0|\beta|n\rangle\ \langle n|\alpha|f\rangle}{-\omega_\alpha-\omega_{nf}}\right]^*$$

$$=M^{\alpha\beta}_{0\leftarrow f}(-\omega_\beta)^*. \tag{4}$$

In coupled cluster response theory a biorthonormal parametrization is used and the transition moments $M^{\alpha\beta}_{f\leftarrow 0}(\omega_\beta)$ and $M^{\alpha\beta}_{0\leftarrow f}(-\omega_\beta)$ are not each others complex conjugate. The symmetry of Eq. (4) therefore holds in coupled cluster response theory not for the individual moments but only for

 © 1998 American Institute of Physics

the transition strengths which are obtained as a symmetrized product of ''left'' $M^{\alpha\beta}_{0\leftarrow f}$ and ''right'' $M^{\alpha\beta}_{f\leftarrow 0}$ transition moments:[2]

$$S^{0f}_{\alpha\beta,\gamma\delta}(\omega)=\tfrac{1}{2}\{M^{\alpha\beta}_{0\leftarrow f}(-\omega)M^{\gamma\delta}_{f\leftarrow 0}(\omega) + M^{\gamma\delta}_{0\leftarrow f}(-\omega)^{*}M^{\alpha\beta}_{f\leftarrow 0}(\omega)^{*}\}. \tag{5}$$

For the transition strength $S^{0f}_{\alpha\beta,\gamma\delta}(\omega)$, which is directly related to a residue of the cubic response function,[2,10] the following symmetries hold:

$$S^{0f}_{\alpha\beta,\gamma\delta}(\omega)=S^{f0}_{\alpha\beta,\gamma\delta}(-\omega)^{*} =S^{0f}_{\gamma\delta,\alpha\beta}(\omega)^{*}=S^{0f}_{\beta\alpha,\delta\gamma}(\omega_{f0}-\omega). \tag{6}$$

In the preceding article,[2] dealing with the derivation of expressions for multiphoton transition moments within the framework of coupled cluster response theory, we showed that the left and right transition moments can be calculated as second derivatives of variational transition moment Lagrangians with respect to the electric field strengths ϵ_α, ϵ_β of the incident light beams:

$$M^{\alpha\beta}_{0\leftarrow f}(\omega_\beta)=\left(\frac{d^2L^{0f}(t,\epsilon)}{d\epsilon_\alpha(\omega_\alpha)d\epsilon_\beta(\omega_\beta)}\right)_0, \quad \omega_\alpha+\omega_\beta=-\omega_f, \tag{7}$$

$$M^{\alpha\beta}_{f\leftarrow 0}(\omega_\beta)=\left(\frac{d^2L^{f0}(t,\epsilon)}{d\epsilon_\alpha(\omega_\alpha)d\epsilon_\beta(\omega_\beta)}\right)_0, \quad \omega_\alpha+\omega_\beta=\omega_f. \tag{8}$$

In coupled cluster response theory, the left and right transition moment Lagrangians for excitations from the ground state 0 to an excited state f are given by:[2]

$$L^{0f}(t,\epsilon)=\lim_{\rho\to 0}e^{\rho t}\left[\eta(t,\epsilon)+\overline{t}(t,\epsilon)\left(\boldsymbol{A}(t,\epsilon)-i\frac{d}{dt}\right)\right] \times E^f(t,\epsilon)+\lim_{\rho\to 0}e^{\rho t}\overline{M}^f(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right), \tag{9}$$

$$L^{f0}(t,\epsilon)=\lim_{\rho\to 0}e^{\rho t}\overline{E^f}(t,\epsilon)\left(e(t,\epsilon)-i\frac{d}{dt}t(t,\epsilon)\right). \tag{10}$$

In Eqs. (9) and (10) $t(t,\epsilon)$ and $\overline{t}(t,\epsilon)$ are the time- and field-dependent ground state cluster amplitudes and Lagrangian multipliers, respectively, $E^f(t,\epsilon)$ and $\overline{E^f}(t,\epsilon)$ are the right and left excited state vectors for state f and $\overline{M}^f(t,\epsilon)$ are left transition moment Lagrangian multipliers. The coupled cluster Jacobian $\boldsymbol{A}(t,\epsilon)$ and the vectors $\eta(t,\epsilon)$ are defined as partial derivatives of the ground state coupled cluster quasienergy and quasienergy Lagrangian. For details about the definitions of these intermediates we refer to Ref. 2. The formulation of transition moments as derivatives of variational functionals allows us to use the framework of variational perturbation theory including the $2n+1$ and $2n+2$ rules[3,4] to derive computational efficient expressions which require the solution of a minimal number of response equations. As shown in Ref. 2, the left and right two-photon transition moments can be calculated as

$$M^{\alpha\beta}_{0\leftarrow f}(\omega_\beta)=\eta^{\alpha\beta}(-\omega_f-\omega_\beta,\omega_\beta)E^f(\omega_f) + \overline{M}^f(\omega_f)\xi^{\alpha\beta}(-\omega_f-\omega_\beta,\omega_\beta), \tag{11}$$

$$M^{\alpha\beta}_{f\leftarrow 0}(\omega_\beta)=\overline{E^f}(-\omega_f)\xi^{\alpha\beta}(\omega_f-\omega_\beta,\omega_\beta) \tag{12}$$

with

$$\eta^{\alpha\beta}(\omega_\alpha,\omega_\beta)=\hat{P}^{\alpha\beta}(\omega_\alpha,\omega_\beta)(\tfrac{1}{2}\boldsymbol{G}t^\alpha(\omega_\alpha)t^\beta(\omega_\beta) + \boldsymbol{F}^\alpha t^\beta(\omega_\beta)+\overline{t^\beta}(\omega_\beta)\boldsymbol{B}t^\alpha(\omega_\alpha) + \overline{t^\beta}(\omega_\beta)\boldsymbol{A}^\alpha), \tag{13}$$

$$\xi^{\alpha\beta}(\omega_\alpha,\omega_\beta)=\hat{P}^{\alpha\beta}(\omega_\alpha,\omega_\beta)(\tfrac{1}{2}\boldsymbol{B}t^\alpha(\omega_\alpha)t^\beta(\omega_\beta) + \boldsymbol{A}^\alpha t^\beta(\omega_\beta)). \tag{14}$$

The vectors t^α, t^β and $\overline{t^\alpha}$, $\overline{t^\beta}$ are the first-order response of the ground state cluster amplitudes and Lagrangian multipliers and α and β index the components of the dipole operator: $\alpha,\beta=x,y,z$. For the definition of the matrices $\boldsymbol{B}$, $\boldsymbol{G}$, $\boldsymbol{F}^\alpha$ and $\boldsymbol{A}^\alpha$ we refer to Refs. 2 and 11. After the solution of the cluster equations for the ground state energy, the calculation of a complete dipole two-photon transition strength tensor $S^{0f}_{\alpha\beta,\gamma\delta}(\omega)$ thus requires the solution of the eigenvalue equations for the left and right eigenvectors $\overline{E^f}$, E^f for state f, the zeroth-order response equations for the ground and transition Lagrangian multipliers $\overline{t^{(0)}}$, $\overline{M}^f$ and the six sets of first-order response equations for $t^\alpha(\omega)$, $t^\alpha(\omega_f-\omega)$, $t^\alpha(-\omega)$, $t^\alpha(-\omega_f+\omega)$, $\overline{t^\alpha}(-\omega)$, and $\overline{t^\alpha}(-\omega_f+\omega)$ with $\alpha=x,y,z$.

III. COMPUTATIONAL DETAILS

The two-photon transition probability rate constant is given by:[1,12]

$$K_{0-f}=a_0^4t_0(2\pi)^2\alpha^2\omega_1\omega_2\delta^{TP}, \tag{15}$$

where a_0 is the Bohr radius, t_0 the atomic unit for time, α the fine structure constant and ω_1 and ω_2 the photon energies (in a.u.). δ^{TP} is a rotationally averaged two-photon transition strength (in a.u.) defined as:[13]

$$\delta^{TP}=F\,\delta_F+G\,\delta_G+H\,\delta_H, \tag{16}$$

$$\delta_F=\frac{1}{30}\sum_{\alpha\beta}S^{0f}_{\alpha\alpha\beta\beta}, \tag{17}$$

$$\delta_G=\frac{1}{30}\sum_{\alpha\beta}S^{0f}_{\alpha\beta\alpha\beta}, \tag{18}$$

$$\delta_H=\frac{1}{30}\sum_{\alpha\beta}S^{0f}_{\alpha\beta\beta\alpha}. \tag{19}$$

The coefficients F, G, and H depend on the polarization of the incident light beams. For parallel linearly polarized laser beams the appropriate values are $F=G=H=2$.[14] The summation in Eqs. (16)–(19) is over the components of the dipole operator $\alpha,\beta=x,y,z$.

Little is known about the basis set requirements for two-photon transition moment calculations, but from the definition Eq. (1) it follows that a basis set should be chosen which is flexible enough to provide a balanced

TABLE I. Excitation energies to the lowest excited singulett states in the atoms He, Ne and Ar (in eV).

State	SCF	CCS	CC2	CCSD	MCSCF	Exp.
Helium						
$1s^1 2s^1$ ($^1S^e$)		21.137	20.790	20.615		20.615 [c]
$1s^1 2p^1$ ($^1P^o$)		21.696	21.389	21.213		21.217 [c]
$1s^1 3s^1$ ($^1S^e$)		23.380	23.044	22.951		22.920 [c]
$1s^1 3p^1$ ($^1P^o$)		23.649	23.320	23.209		23.086 [c]
$1s^1 3d^1$ ($^1D^e$)		23.781	23.498	23.376		23.073 [c]
Neon						
$2p^5 3s^1$ ($^1P^o$)		18.352	16.094	16.739		16.848 [c]
$2p^5 3p^1$ ($^1D^e$)	20.106 [a]	20.110	17.767	18.532	18.874 [a]	18.637 [c]
$2p^5 3p^1$ ($^1P^e$)		20.148	17.805	18.578		18.694 [c]
$2p^5 3p^1$ ($^1S^e$)		20.586	17.945	18.855		18.966 [c]
Argon						
$3p^5 4s^1$ ($^1P^o$)	12.200 [b]	12.210	11.803	11.843	11.816 [b]	11.828 [c]
$3p^5 4p^1$ ($^1D^e$)	13.485 [b]	13.489	13.131	13.218	13.185 [b]	13.171 [c]
$3p^5 4p^1$ ($^1P^e$)		13.567	13.194	13.285	13.277 [b]	13.282 [c]
$3p^5 4p^1$ ($^1S^e$)	13.770 [b]	13.807	13.340	13.487	13.435 [b]	13.480 [c]

[a]Reference 6.
[b]Reference 12.
[c]Reference 24.

treatment of the ground state and the excited state wave functions and their first-order corrections due to perturbation by an electric field. In the calculations we used the triply augmented polarized correlation consistent valence quintuple zeta (t-aug-cc-pV5Z) basis sets[15] for helium $(11s7p6d5f4g)/[8s7p6d5f4g)$, neon $(17s11p7d6f5g4h)/[9s8p7d6f5g4h]$ and argon $(23s15p7d6f5g4h)/[10s9p7d6f5g4h]$. In the calculations for neon and argon only the eight valence electrons were correlated.

IV. RESULTS AND DISCUSSION

In Table I we have compiled the calculated excitation energies for the first few lowest excited singlet states of the rare gas atoms helium, neon and argon. As demonstrated in previous studies,[16,17] we obtain at each higher level of the coupled cluster hierachy CCS, CC2 and CCSD a significant improvement of the excitation energies. At the CCSD level we find for these atoms in general a close agreement with experiment. The sources of the remaining errors are very different for the three atoms: for helium we have the full CI limit results and the remaining errors are due to basis set defects, for neon and argon the contributions from connected triples and higher excitation levels are neglected and are the major source of errors. For helium we find somewhat larger errors between 0.03–0.30 eV for the excitations to the 3-shell ($1s^1 3s^1$, $1s^1 3p^1$, $1s^1 3d^1$). These excitations are less accurately described by the t-aug-cc-pV5Z basis. This is of course a consequence of the fact that the basis was optimized for the ground state correlation energy, but not for excited states. For argon, the neglect of the spin-orbit interaction leads to additional errors. However, for argon the effect of electron correlation on the calculated four excitation energies is relatively small and we obtain at the CCSD level a maximum error of 0.047 eV for the $^1S^e \rightarrow {}^1D^e$ transition. Already on the CC2 level we have obtained an accuracy of 0.025 – 0.14 eV, while for neon the errors are about $\sim$0.9 eV at the CC2 level and about 0.1 eV for CCSD. The mean absolute and the maximum errors of the calculated CCSD excitation energies for the three atoms are 0.07 and 0.30 eV, respectively, where the largest error is found for the excitation to the $1s^1 3d^1(^1D^e)$ state in helium. If we compare the CCSD excitation energies for argon with the CASSCF results of Ref. 12, we find that the errors in both calculations are of the same order of magnitude.

In the sum over states definition Eq. (1), the two-photon transition moment is formally obtained as the sum of the dipole transition moments between the ground state 0 and intermediates states n, multiplied by the dipole transition moment between the intermediate states and the final state f,

TABLE II. The one-photon dipole oscillator strengths between the ground state and the lowest $^1P^e$ state in He, Ne and Ar.

Method	$f_{X\ ^1S^e\text{-}^1P^e}$
Helium	
CCS	0.2554
CC2	0.2649
CCSD	0.2766
Exp.	0.280 ± 0.007 [a]
Neon	
CCS	0.1666
CC2	0.1570
CCSD	0.1650
Exp.	0.171 ± 0.008 [b]
Argon	
SCF	0.3154 [c]
CCS	0.3228
CC2	0.3229
CCSD	0.3219
CAS	0.3358 [c]
Exp.	0.331 ± 0.016 [d]

[a]Reference 18.
[b]Reference 19.
[c]Reference 12.
[d]Reference 20.

TABLE III. The two-photon transition strengths and rate constants between the ground state and the $^1S^e$ state in He.

	$\omega_1=\omega_2=\frac{1}{2}\omega_{f0}$		$\omega_2=10.49$ eV	
Method	S^{0f}/a.u.	K_{0-f}/cm^4 s	S^{0f}/a.u.	K_{0-f}/ cm^4 s
CCS	10.824	0.4091×10^{-51}	10.826	0.4091×10^{-51}
CC2	11.617	0.4247×10^{-51}	11.619	0.4248×10^{-51}
CCSD	12.306	0.4424×10^{-51}	12.315	0.4426×10^{-51}

divided by an energy difference. In the *ab initio* response theory approaches, the sum over intermediate states is expressed in terms of solutions to linear equations in order to obtain computationally tractable expressions. However, the *ab initio* method and the basis set which have been chosen must be able to provide an accurate representation of at least the most important intermediate states. For two-photon transitions from the ground state to the $^1S^e$ state in helium and the $^1S^e$ and the $^1D^e$ states in neon and argon the dominating contributions originate from the lowest $^1P^o$ states in these atoms. We have already shown that the coupled cluster response approach gives at the CCSD level accurate excitation energies for the transitions to the $^1P^o$ states. To obtain further insight, we computed the dipole transition strengths for the ground state to $^1P^o$ transitions in He, Ne, and Ar. A comparison of the CCS, CC2 and CCSD results with the SCF and complete active space SCF (CAS) results of Refs. 6, 12 and the experimental values from Refs. 18–20 is given in Table II. To compare with experiment, we added the experimental values for the $P_{1/2}$ and $P_{3/2}$ contributions. For all three atoms we obtain at the CCSD level oscillator strengths for the $X\ ^1S^e\rightarrow\ ^1P^e$ transition within the experimental uncertainities.

In Tables III-V we have listed the two-photon transition strengths and the transition probability rate constants obtained with CCS, CC2 and CCSD for the cases with $\omega_1=\omega_2=\frac{1}{2}\omega_{f0}$ and for the case $\omega_2=10.49$ eV$=0.3855$ a.u. (the experimental laser frequency used for argon[21–23]) and $\omega_1=\omega_f-\omega_2$. If we compare the rate constants for the $X\ ^1S^e\rightarrow\ ^1S^e$ and $X\ ^1S^e\rightarrow\ ^1D^e$ transitions for $\omega_1=\omega_2$ for the three atoms, we find an increase of the rate constant K_{0-f} from helium to neon and argon by a factor of ≈1.5 and ≈4 to 5. The large increase in the two-photon transition probability from neon to argon is even more pronounced for $\omega_2=10.49$ eV, because in this case ω_2 comes close to the $X\ ^1S^e\rightarrow\ ^1P^e$ excitation energy in argon. The effect of electron correlation on the two-photon transition strengths varies significantly for the three atoms and also with the different frequencies. For helium and also for the $\omega_1=\omega_2$ case in argon, electron correlation has only a moderate effect on the transition strengths, but for neon and also for the $\omega_2=10.49$ eV case in argon the inclusion of electron correlation has a drastic effect on the results with differences of about 50% between the CCS and the CCSD results. In the cases where the effects of electron correlation are small, the CC2 results are good approximations to the CCSD values, but in the cases with large correlation effects CC2 overshoot the CCSD value considerably by 10%–25%. For the $X\ ^1S^e\rightarrow\ ^1D^e$ transitions in neon and argon, recent MCSCF quadratic response results are available.[12,6] For both atoms the agreement between the CCSD and the MCSCF results is good. For argon we can compare with the experimental transition probability rate constant for the transition to the $^1D^e$ state[12] derived as the sum of the transition probability rates to the spin-orbit mixed states $3p^5(^2P^o_{3/2})4p[3/2]_{J=2}(^1D^e)$, $3p^5(^2P^o_{3/2})4p[5/2]_{J=2}(^3D^e)$, and $3p^5(^2P^o_{3/2})4p[3/2]_{J=2}(^3P^e)$. The resulting experimental value of 2.05×10^{-51} cm^4 s agrees well with the CCSD result of 1.83×10^{-51} cm^4 s, considering the uncertainity introduced by neglecting the spin-orbit coupling.

TABLE IV. The two-photon transition strengths and rate constants between the ground state and the $^1S^e$ and $^1D^e$ states in Ne.

	$\omega_1=\omega_2=\frac{1}{2}\omega_{f0}$		$\omega_2=10.49$ eV	
Method	S^{0f}/a.u.	K_{0-f}/cm^4 s	S^{0f}/a.u.	K_{0-f}/ cm^4 s
$2p^53p^1$ ($^1S^e$)				
CCS	12.559	0.450×10^{-51}	12.575	0.451×10^{-51}
CC2	23.108	0.629×10^{-51}	25.377	0.672×10^{-51}
CCSD	19.915	0.599×10^{-51}	20.793	0.617×10^{-51}
$2p^53p^1$ ($^1D^e$)				
SCF	8.799[a]	0.0690×10^{-51}[b]		
CCS	8.737	0.0797×10^{-51}	8.798	0.0801×10^{-51}
CC2	12.753	0.0908×10^{-51}	14.528	0.1001×10^{-51}
CCSD	12.024	0.0931×10^{-51}	12.876	0.0980×10^{-51}
MCSCF	11.289[a]	0.0885×10^{-51}[b]		

[a]Reference 6.

[b]Calculated from the two-photon transition moments of Ref. 6 assuming $\omega_1=\omega_2=0.3425$ a.u.

TABLE V. The two-photon transition strengths and rate constants between the ground state and the $^1S^e$ and $^1D^e$ states in Ar.

	$\omega_1=\omega_2=\frac{1}{2}\omega_{f0}$		$\omega_2=10.49$ eV	
Method	S^{0f} / a.u.	K_{0-f} / cm^4 s	S^{0f} / a.u.	K_{0-f} / cm^4 s
$2p^5 3p^1$ ($^1S^e$)				
CCS	165.40	2.67×10^{-51}	571.61	6.73×10^{-51}
CC2	201.89	3.04×10^{-51}	984.24	9.96×10^{-51}
CCSD	197.71	3.04×10^{-51}	894.78	9.52×10^{-51}
$2p^5 3p^1$ ($^1D^e$)				
SCF	90.23[a]	0.370×10^{-51}[a]	418.90[a]	1.19×20^{-51}
CCS	95.15	0.391×10^{-51}	446.23	1.27×10^{-51}
CC2	104.15	0.405×10^{-51}	768.16	1.92×10^{-51}
CCSD	104.59	0.412×10^{-51}	708.61	1.83×10^{-51}
MCSCF	108.66[a]	0.426×10^{-51}[a]	748.95[a]	1.91×10^{-51}[a]
Exp.				2.05×10^{-51}[b]

[a]Reference 12.
[b]References 12, 21–23.

V. SUMMARY

We have reported an implementation of two-photon transition moments for the hierachy of coupled cluster models CCS, CC2 and CCSD. In coupled cluster response theory, the two-photon transition strength is obtained as a symmetrized product of left and right transition moments. The coupled cluster expression for the transition strength satisfies the same symmetries with respect to complex conjugation and permutation of the transition operators as the exact transition strength. Applications to the probability rate constants for the transitions from the ground state to the first excited $^1S^e$ state in helium and to the lowest $^1D^e$ and $^1S^e$ state in neon and argon demonstrate a good performance of the coupled cluster model hierachy CCS, CC2 and CCSD for the calculation of two-photon transition moments. The CCS model gives results of a similar accuracy as SCF or RPA. The CCSD results are close to the best available MCSCF results and close to the experimental value for argon. In cases with modest correlation effects the CC2 model gives results close to the CCSD values, but in cases with larger correlation effects CC2 overshoots the CCSD results.

ACKNOWLEDGMENTS

One of the authors (C.H.) thanks the European Commission for financial support through the Training and Mobility of Researchers (TMR) Programm (ERBFMBICT 96.1066). This work has been supported by the Danish Natural Research Council (Grant No. 9600856).

[1] M. Göpper-Mayer, Ann. Phys. (Leipzig) **9**, 273 (1931).
[2] C. Hättig, O. Christiansen, and P. Jørgensen, J. Chem. Phys. **108**, 8331 (1998), preceding paper.
[3] T. Helgaker and P. Jørgensen, Theor. Chim. Acta **75**, 111 (1989).
[4] P. Jørgensen and T. Helgaker, J. Chem. Phys. **89**, 1560 (1988).
[5] R. Moccia and A. Rizzo, Mol. Phys. **51**, 1095 (1984).
[6] H. Hettema, H. J. Å Jensen, P. Jørgensen, and J. Olsen, J. Chem. Phys. **97**, 1174 (1992).
[7] O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).
[8] H. Koch, O. Christiansen, P. Jørgensen, A. Sánchez de Merás, and T. Helgaker, J. Chem. Phys. **106**, 1808 (1997).
[9] O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **103**, 7429 (1995).
[10] J. Olsen and P. Jørgensen, J. Chem. Phys. **82**, 3235 (1985).
[11] O. Christiansen, P. Jørgensen, and C. Hättig, Int. J. Quantum Chem. (to be published).
[12] D. Sundholm, A. Rizzo, and P. Jørgensen, J. Chem. Phys. **101**, 4931 (1994).
[13] P. R. Monson and W. M. McClain, J. Chem. Phys. **53**, 29 (1979).
[14] R. Moccia and A. Rizzo, J. Phys. B **18**, 3319 (1985).
[15] D. E. Woon and T. H. Dunning, J. Chem. Phys. **103**, 4572 (1995). The basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, and funded by the U.S. Department of Energy. PNL is a multiprogram laboratory operated by Batelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830.
[16] H. Koch, O. Christiansen, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **244**, 75 (1995).
[17] O. Christiansen, H. Koch, P. Jørgensen, and Jeppe Olsen, Chem. Phys. Lett. **256**, 185 (1996).
[18] W. F. Chan, G. Cooper, and C. E. Brion, Phys. Rev. A **44**, 186 (1991).
[19] W. F. Chan, G. Cooper, X. Guo, and C. E. Brion, Phys. Rev. A **45**, 1420 (1992).
[20] W. F. Chan, G. Cooper, X. Guo, G. R. Burton, and C. E. Brion, Phys. Rev. A **46**, 149 (1992).
[21] M. G. Payne, C. H. Chen, G. S. Hurst, and G. W. Foltz, *Advances in Atomic and Molecular Physics* (Academic, New York, 1981), Vol. 17, pp. 229–274.
[22] M. P. McCann, C. H. Chen, and M. G. Payne, J. Chem. Phys. **89**, 5429 (1989).
[23] M. G. Payne, C. H. Chen, G. S. Hurst, S. D. Kramer, W. R. Garrett, and M. Pindzola, Chem. Phys. Lett. **79**, 142 (1981).
[24] C. E. More, Atomic Energy Levels (U.S. Natl. Bur. Stand., Washington, 1949), Circular 467, Vol. I.