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Calculation of total photoabsorption cross sections of Ar, Kr, N_2 and CO [1]

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Abstract

We present a new inversion procedure for the dispersion integral equation relating the total photoabsorption cross section to the frequency-dependent (dynamic) polarizability of an atom or molecule. Together with a reliable method to calculate the latter, this opens a way to the calculation of photoabsorption cross sections for complex molecules. We assess the reliability of the new inversion method by inverting the response functions for Ar, Kr, N_2 and CO as obtained by the time-dependent second-order Møller-Plesset method and comparing with other theoretical and experimental results. © 1997 Elsevier Science B.V.

1. Introduction

Over the past two decades the computation of photoabsorption cross sections for molecules has been an active field of research. A reliable calculation of the continuum orbitals of the outcoming electron has proven as one of the major difficulties. Another complication is associated with correlation effects in the initial and final electronic state of the system, which turned out to be far from negligible.

For the case of atoms sophisticated methods have been developed to treat these two problems [1,2]. These methods, however, cannot be easily applied to molecules due to the difficulty of constructing continuum orbitals for a multicenter system. For light diatomic hydrides, like OH, CH and FH, satisfactory results can be achieved in terms of a single-center expansion [3–5]. For large molecules or homonuclear diatomics (e.g., N_2) such an expansion ceases to be useful. Standard approaches to treat these systems rely on the so-called Stieltjes-imaging method [6–9] or the K-matrix RPA (Random Phase Approximation) [10]. These algebraic approaches do not explicitly take into account continuum orbitals.

There exists an alternative method for the evaluation of the total photoabsorption cross sections which makes use of the electronic structure of the system before the excitation process only, namely its response properties. Cross sections are obtained indirectly by means of dispersion relations: the real part Re $\alpha(\omega)$ of the dynamic polarizability $\alpha(\omega)$ is related to its imaginary part Im $\alpha(\omega)$, which in turn is related to the total photoabsorption cross section. Thus, for any given dynamic polarizability the total photoabsorption cross section can be computed by inverting the corresponding dispersion integral. This method was applied by L. Veseth for calculating both atomic [11] and molecular [12–14] cross sections.

[1] Dedicated to Sigrid Peyerimhoff on occasion of her 60th birthday.

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The aim of this article is to propose a new inversion procedure for the dispersion integral equation and to evaluate its performance in applications to both atomic and molecular systems. We shall not address the problem of computing dynamic polarizabilities, but rather employ the results recently obtained within the Time-dependent Møller-Plesset perturbation theory to second order (TDMP2), a new approach for the calculation of the response function which includes the effects of the electron correlation [15–17]. This method can be used for the calculation of polyatomic molecules as well as for simpler systems, and a reliable inversion procedure for the dispersion integral would open a new way to photoabsorption cross sections of complex molecules.

2. Theoretical concepts

2.1. Dynamic polarizability and photoabsorption cross section

The behavior of an atomic or molecular system under the influence of an external perturbation (in our case the interaction with monochromatic light) is to first order determined by the frequency-dependent (dynamic) polarizability [18,19]. In general, the dynamic polarizability $\alpha(\omega)$ is a complex function depending on a complex variable ω, the imaginary part of which will be denoted by $i\eta$ in the following. It can be shown [18] that $\alpha(\omega)$ is purely real on the imaginary axis.

From the analytic properties of $\alpha(\omega)$ one can derive a dispersion or Kramers-Krönig relation, which for $\alpha(i\eta)$ has the form

$$\alpha(i\eta) = \frac{2}{\pi}\int_0^\infty \frac{\omega\,\mathrm{Im}\,\alpha(\omega)}{\omega^2+\eta^2}\,\mathrm{d}\omega. \tag{1}$$

The imaginary part $\mathrm{Im}\,\alpha(\omega)$ is related to the total photoabsorption cross section by

$$\mathrm{Im}\,\alpha(\omega) = \frac{c}{4\pi}\frac{\sigma(\omega)}{\omega}, \quad \omega > 0. \tag{2}$$

Hence, Eq. (1) can be written as

$$\alpha(i\eta) = \frac{c}{2\pi^2}\int_0^\infty \frac{\sigma(\omega)}{\omega^2+\eta^2}\,\mathrm{d}\omega. \tag{3}$$

2.2. Methods of integral inversion

For the subsequent discussion of the methods of inversion of Eq. (3), we write it in the generic form of an integral transform

$$d(x) = \frac{c}{2\pi^2}\int_0^\infty \frac{g(t)}{t^2+x^2}\,\mathrm{d}t. \tag{4}$$

2.2.1. Expansion of the cross section in a set of basis function

The method used by Veseth [11] to invert Eq. (4) is based on expanding $g(t)$ in a complete set of known basis functions [20]. In practice, the expansion has to be restricted to a finite number of functions:

$$g(t) = \sum_{n=1}^{N} a_n \chi_n(t). \tag{5}$$

With this ansatz, Eq. (4) becomes

$$d(x) = \frac{c}{2\pi^2}\sum_{i=1}^{N} a_n h_n(x) \tag{6}$$

with

$$h_n(x) = \int_0^\infty \frac{\chi_n(t)}{t^2+x^2}\,\mathrm{d}t. \tag{7}$$

The inversion problem now consists of finding a set of N linearly independent functions $h_n(x)$. Veseth employs exponential trial functions for the χ_n, weighted with a factor t^3 to impose the correct asymptotic behavior for $t \to \infty$ and $t \to 0$:

$$\chi_n(t) = t^3\,\mathrm{e}^{-k_n t}. \tag{8}$$

The (numerical) linear independence of these basis functions is ensured by choosing the exponents of the form

$$k_n = k_0 C^{n-1} \tag{9}$$

with a real constant $C > 1$.

2.2.2. Stieltjes transform

In order to devise an alternative inversion method, we rewrite the integral transform Eq. (4) and substitute $\tilde{x} = x^2$, $\tilde{t} = t^2$, resulting in

$$d(\sqrt{\tilde{x}}) = \frac{c}{2\pi^2}\int_0^\infty \frac{\tilde{g}(\tilde{t})}{\tilde{x}+\tilde{t}}\,\mathrm{d}\tilde{t}, \quad \tilde{g}(\tilde{t}) = \frac{g(t)}{2t}. \tag{10}$$

Integral equations with this kernel are known as Stieltjes transforms [21–23], and pairs of functions related by the Stieltjes transform are collected in the corresponding tables of integral transforms [24]. This opens the possibility to choose as expansion functions according to Eqs. (5) and (6) families of functions which are related by the exact property of being transformation pairs $h_n(\tilde{x}) = S\left[\tilde{\chi}_n(\tilde{t})\right]$, $S[.]$ denoting the Stieltjes transform, and looking up the inverse transform $S^{-1}[.]$ from the tables. The number of function pairs may be considerably increased by noting that $S[.] = L[L[.]]$, i.e., the Stieltjes transform may be considered as an iterated Laplace transform [25].

Although the integral transformation approach gives considerable flexibility, we had considerable difficulties in finding a familiy of functions $\{\chi_n\}$ leading to a satisfactory description of $\sigma(\omega)$ over the whole ω range considered. Moreover, it is still necessary to fit the m known points $\alpha(i\eta_k)$, $k = 1, \ldots, m$ in a non-linear fit procedure [26] to a set of functions $\{h_n\}$ which might or might not be well-adapted to the functional form of the physical quantities. As a third approach, we therefore consider the numerical inversion of the transformation (10) making use of a linear fit procedure.

2.2.3. Potential transform

From the theory of integral transforms [27] an inversion procedure for integral equations of the form

$$d(x) = \frac{2}{\pi}\int_0^\infty \frac{t\phi(t)}{x^2 + t^2}\,\mathrm{d}t, \tag{11}$$

dubbed the 'potential transform', is available. If the function $d(x)$ has a power series expansion convergent for some positive $|x| < \rho$,

$$d(x) = \sum_{k=0}^{\infty} a_k x^{k-\beta}, \quad 0 < x < \rho, \tag{12}$$

with fixed $\beta \in \Re$, then the inverse function can be written as

$$\phi(t) = \sum_{k=0}^{\infty} a_k t^{k-\beta} \sin\frac{\pi}{2}(\beta - k), \quad 0 < t < \delta, \tag{13}$$

a convergent power series for some $\delta > 0$. The same technique may be used if an expansion at infinity is employed, in which case the power series of $d(x)$ reads

$$d(x) = \sum_{k=0}^{\infty} b_k \left(\frac{1}{x}\right)^{k+\beta}, \quad \rho < x < \infty, \tag{14}$$

and $\phi(t)$ is given as

$$\phi(t) = \sum_{k=0}^{\infty} b_k \left(\frac{1}{t}\right)^{k+\beta} \sin\frac{\pi}{2}(\beta + k), \quad R < t < \infty \tag{15}$$

for some R.

Since Eq. (4) may be easily brought to the form of Eq. (11), a numerical inversion procedure based on a linear fit may be readily devised based on this technique. Since, however, $\alpha(\omega)$ is expected to have poles on the real axis, the meaning of a polynomial approximation has to be discussed very carefully. Obviously, any polynomial approximation can be valid only on a finite interval.

The idea is to approximate $d(x)$ on a suitably chosen interval $[x_{\min}, x_{\max}]$ by some function, which is in turn inverted by means of a power series according to Eq. (13) or Eq. (15), yielding an approximation for $\phi(t)$ on an interval $[t_{\min}, t_{\max}]$. In the simplest case, which will be employed below, we approximate $d(x)$ by a polynomial

$$\tilde{d}(x) = \sum_{k=0}^{k_{\max}} a_k x^{k-\beta} \tag{16}$$

for suitably chosen $k_{\max}$ and β. This polynomial is in turn is interpreted as approximation to the power series of a function $\hat{d}(x)$ with the property that the coefficients a_k for $k > k_{\max}$ are smaller than some threshold that assures that on $[x_{\min}, x_{\max}]$ the functions $d(x)$, $\tilde{d}(x)$ and $\hat{d}(x)$ do not differ appreciably. The inversion according to Eq. (13) then defines a polynomial $\tilde{\phi}(t)$, and we take this function as an approximation for $\phi(t)$ on a physically meaningful interval $[t_{\min}, t_{\max}]$. In practice, we take this interval to range from the first excitation energy of the system to a suitable upper frequency.

The described inversion method may also be used if a sum of functions with point singularities is employed as approximant, since the expansion Eq. (14) can be used beyond the radius of convergence of Eq. (12).

2.3. Technical details

The numerical inversion of the potential transform by means of a polynomial approximant does not require a non-linear fit; we rather determine linear fit parameters $\{a_n\}$ for the expansion (16) and calculate the approximant for $\phi(t)$ according to

$$\tilde{\phi}(t) = \sum_{k=0}^{k_{\max}} a_k t^{k-\beta} \sin\frac{\pi}{2}(\beta - k). \tag{17}$$

We make use of negative powers to account for a proper decrease of $\alpha(i\eta)$ for increasing $i\eta$ values.

Since the *ab initio* calculation for a large number of points would be very time consuming, we rather use the parametrization of the calculated *ab initio* points by means of an effective spectrum

$$d_{\text{eff}}(x) = \sum_m \frac{f_m}{\varepsilon_m^2 + x^2} \tag{18}$$

as an intermediate step. We should like to emphasize that this is a matter of convenience only, motivated by the fact that effective spectra are readily available from the literature. The determination of the effective spectrum requires, of course, again a non-linear fit, and indeed $\{f_m\}$ could in principle be interpreted as the oscillator strength distribution in its own right. Note, however, that the parameters $\{f_m\}$ and $\{\varepsilon_m\}$ in Eq. (18) are unphysical, and are used here only as intermediate quantities, providing a parametrization of $\alpha(i\eta)$ in particular in the asymptotic region $i\eta \to \infty$. The $\{f_m\}$ as determined from such fits indeed do not prove suitable as photoabsorption cross sections. It is easy to see that our inversion procedure described above, when applied directly to Eq. (18), yields immediately oscillator strengths f_m at the energy parameter values ε_m, i. e., $\sigma(\omega) = \sum_m f_m \delta(\omega - \varepsilon_m)$. Thus, the fit to an effective spectrum composed of a finite number of terms is principally not able to describe a continuous photoabsorption cross section, because the spectral density of the continuum does not explicitly enter the representation (18). However, with this representation of $\alpha(i\eta)$ a large number of points on the curve $\alpha(i\eta)$ may be easily calculated, which are then fitted to a polynomial (16) to obtain $\sigma(\omega)$ as described above.

3. Results

In order to test the proposed inversion methods, we make use of dynamic dipole polarizabilities obtained from effective spectra in the literature [16,17], which are calculated by the time-dependent second-order Møller-Plesset method (TDMP2) [15]. Within this method, the dynamic polarizabilities are defined as analytic second derivatives of the second-order Møller-Plesset (MP2) energy with respect to the strenghts of two oscillating external fields. Thus, the effects of electron correlation are included to second order in perturbation theory defined with respect to orbitals which are themselves perturbed by the external electromagnetic field causing the photoabsorption process.

Formally, the quantity $\sigma(\omega)$ corresponds to the total photoabsorption cross section. For atoms it can be shown [28] that the contribution of the discrete absorption spectrum is practically neglible. Therefore, the computed results for $\sigma(\omega)$, obtained by inverting Eq. (3), can in this case be regarded as total photoionization cross sections.

3.1. Total photoionization cross section of argon and krypton

Applying two families of functions which are related by a Stieltjes transform according to Section 2.2.2, we selected as expansion functions for the cross section

$$g_n(y) = a_n \frac{y^2}{b_n^4 + y^4} \tag{19}$$

which posesses the Stieltjes transform

$$d_n(x) = a_n \frac{\pi}{2} \frac{1}{b_n^4 + x^4} \left[\frac{1}{\sqrt{2}\, b_n} \left(b_n^2 + x^2 \right) - x \right]. \tag{20}$$

The choice of the ansatz function was motivated by the gross features of the functional form of $\sigma(\omega)$. For the calculation of the cross section a fit of the parameters a_n and b_n is needed. To avoid linear dependencies, the b_n's are taken as

$$b_n = b_0^1 + b_0^2(2n - 1) \tag{21}$$

Table 1
The total photoionisation cross section for Ar as function of the photon energy ω; results are computed with both inversion of the Stieltjes transform (ST) and polynomial inversion of the potential transform (PT)

ω [a.u.]	$\sigma(\omega)^{ST}$ [Mb]	$\sigma(\omega)^{PT}$ [Mb]	Exp. [34]
0.60	28.3	31.9	31.1
0.70	36.3	38.8	36.3
0.80	37.5	36.9	36.3
0.90	33.3	31.7	33.5
1.00	26.9	25.8	28.9
1.20	15.5	15.5	17.1
1.40	8.8	8.2	5.7
1.60	5.3	3.4	1.5
1.80	3.5	0.7	0.9

Table 2
The total photoionisation cross section for Kr as function from the photon energy ω; results are computed with inversion of the Stieltjes transform (ST) and polynomial inversion of the potential transform (PT)

ω [a.u.]	$\sigma(\omega)^{ST}$ [Mb]	$\sigma(\omega)^{PT}$ [Mb]	Exp. [34]
0.51	36.7	42.9	29.6
0.56	40.8	46.8	41.8
0.59	41.9	47.4	42.9
0.68	40.5	44.4	40.6
0.77	35.5	38.4	36.4
0.86	29.9	31.9	31.4
1.01	22.2	22.4	24.5
1.38	11.8	7.9	6.6
1.82	6.8	1.2	1.7

with $b_0^1 = b_0^2 = 1$ for argon and $b_0^1 = \frac{2}{3}$, $b_0^2 = 1.43$ for krypton. For both atoms a set of five basis functions is chosen. The parameters for the effective spectra of Ar and Kr are taken from [16].

The results for the photoionization(absorption) cross sections calculated with both inversion techniques, subsequently characterized by the interpretation of the integral equation as 'Stieltjes transform' or 'potential transform', respectively, are listed in Tables 1 and 2 and displayed in Figs. 1 and 2. As mentioned in Ref. [11], several theoretical results for the total photoionization cross section of noble gas atoms are available in the literature. We compare our results in particular with those of Veseth [11] and the Hartree-Fock calculations by Kennedy and Manson [29]. The inversion by Stieltjes transform gives a very accurate representation of the region arround the maximum for both argon and krypton cross

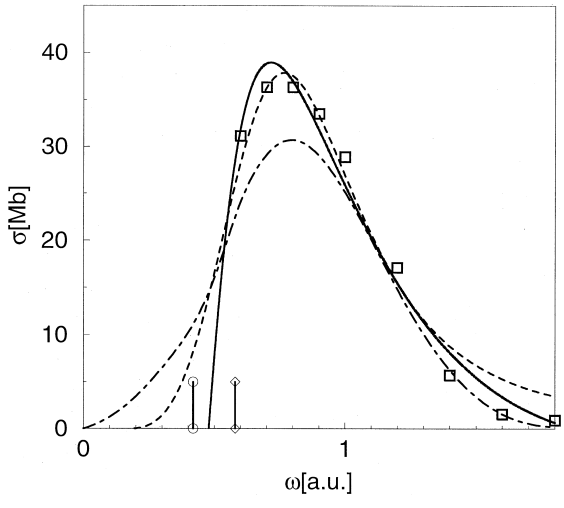


Fig. 1. Total photoionization cross section for Ar: results obtained from polynomial inversion of the potential transform (solid line), inversion of the Stieltjes transform (dashed line), with Veseth's ansatz (Section 2.2.1) [11] (dot-dashed line) and experimental data (□) [34]. The first vertical line (○–○) indicates the energies of the first excited state $3p^5 4s$ at $\omega = 0.42$ a.u., the second one (◇–◇) marks the photoionization threshold at $\omega = 0.58$ a.u..

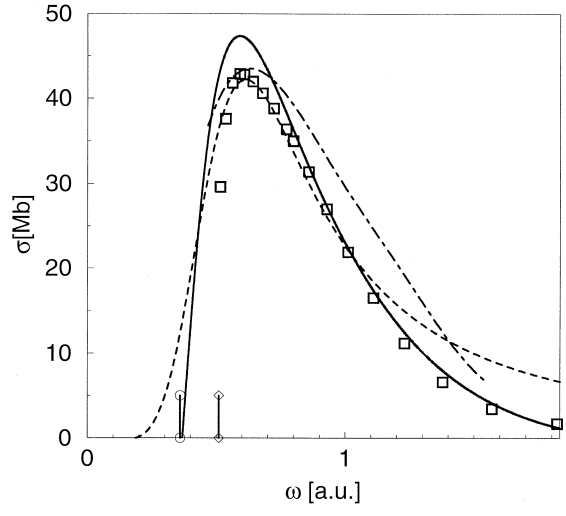


Fig. 2. Total photoionization cross section for Kr: results by polynomial inversion of the potential transform (solid line), inversion of the Stieltjes transform (dashed line), Hartree-Fock (length-form) results [29] (dot-dashed line) and experimental data (□) [34]. The first vertical line (○–○) indicates the energy of the first excited state $4p^5 5s$ at $\omega = 0.36$ a.u., the second one (◇–◇) marks the photoionization threshold at $\omega = 0.51$ a.u..

Table 3
The numerical parameters for the calculation of the atomic cross sections by polynomial inversion of the potential transform; p denotes the number of points employed in the fit. For an explanation of the other parameters see Section 2.3

	k_{max}	β	x_{min}	x_{max}	p
Ar	12	16	0.05	55	1100
Kr	11	16	0.05	55	3800

sections, but fails for the description at higher energies, e.g., it increases too slowly for large ω, while Veseth's results obtained with the exponential functions at least for argon decrease to rapidly with ω. This clearly exhibits the deficiency of an inversion procedure which depends on a particular ansatz function.

An appreciable improvement of the inversion procedure is realized by means of the polynomial inversion of the potential transform. The results obtained with this method lead to a balanced description of the cross sections over the entire region of physical interest. The cross section for krypton is slightly overestimated as compared to the experimental results. We attribute this fact to the known overestimation of correlation effects in $\alpha(i\eta)$ by the TDMP2 method [16]. The results obtained with the polynomial inversion of the potential transform also lead to a realistic onset of the photoabsorption cross section near the first excited state, at variance with the other approaches.

3.2. Total photoionization cross section of nitrogen and carbon monoxide

We now turn to the calculation of total photoabsorption cross sections for the molecules N_2 and CO. Since the TDMP2 approach is not restricted to diatomics, the method can easily be generalized to more complex molecules. The isotropic polarizability $\alpha(i\eta)$ of linear molecules is given by

$$\alpha(i\eta) = \tfrac{1}{3}\{2\alpha_{\perp}(i\eta) + \alpha_{\parallel}(i\eta)\}. \qquad (22)$$

The two components $\alpha_{\perp}(i\eta)$ und $\alpha_{\parallel}(i\eta)$ have both been computed with fixed internuclear distances [17] ($R_{C-O} = 2.132$ a.u. and $R_{N-N} = 2.07$ a.u.). In the last section it was demonstrated that the numerical inversion based on the polynomial inversion of the potential transform is superior to the alternative inversion by Stieltjes transform. Therefore, the molecular calculations are only performed with the numerical inversion method. The inversion is carried out with both components of the dynamic polarizability separately. The parameters f_m and ε_m characterizing the effective spectra can be found in Ref. [17]. The calculated numerical parameters are given in Tables 3 and 4.

Table 4
The numerical parameters for the calculation of the molecular cross sections by polynomial inversion of the potential transform; p denotes the number of points employed in the fit, x_{min} was set to x_{max}/p throughout. For an explanation of the other parameters see Section 2.3

		k_{max}	β	x_{max}	p
N_2	$\alpha^{\perp}$	10	14	75	2000
	$\alpha^{\parallel}$	9	14	75	2100
CO	$\alpha^{\perp}$	9	14	75	2050
	$\alpha^{\parallel}$	10	12	75	3500

The computed results for the total cross sections of N_2 and CO, taking both components of $\alpha(i\eta)$ and

Table 5
The two components $\sigma(\omega)^{\perp}$ and $\sigma(\omega)^{\parallel}$ of the total N_2-photoionization cross section $\sigma(\omega) = \sigma(\omega)^{\perp} + \sigma(\omega)^{\parallel}$ depending on the photon energy ω computed by polynomial inversion of the potential transform

ω [a.u.]	$\sigma(\omega)^{\perp}$ [Mb]	$\sigma(\omega)^{\parallel}$ [Mb]	Exp. [35]
0.60	16.3	13.0	24.9
0.70	15.4	11.8	23.8
0.73	15.1	11.3	22.6
0.77	14.7	10.7	22.0
0.81	14.3	10.0	22.7
0.84	14.1	9.6	24.7
0.90	13.5	8.8	24.1
0.95	13.1	8.1	22.7
1.10	12.0	6.5	20.8
1.25	11.1	5.3	16.4
1.40	10.2	4.4	13.4
1.54	9.4	3.7	11.5
1.70	8.5	3.1	10.9
1.83	7.9	2.7	9.9
1.98	7.1	2.3	8.6
2.13	6.4	1.9	7.5
2.28	5.6	1.7	6.2
2.42	4.9	1.4	5.1
2.53	4.4	1.3	5.3

Table 6
The two components $\sigma(\omega)^{\perp}$ and $\sigma(\omega)^{\parallel}$ of the total CO-photoionization cross section $\sigma(\omega)=\sigma(\omega)^{\perp}+\sigma(\omega)^{\parallel}$ depending on the photon energy ω computed by polynomial inversion of the potential transform

ω [a.u.]	$\sigma(\omega)^{\perp}$ [Mb]	$\sigma(\omega)^{\parallel}$ [Mb]	Exp. [35]
0.66	15.7	10.6	25.9
0.70	15.5	9.9	23.6
0.73	15.2	9.3	23.3
0.77	14.7	8.8	23.9
0.81	14.3	8.2	24.1
0.84	13.9	7.8	23.7
0.90	13.5	7.1	23.4
0.95	12.6	6.6	23.1
1.10	11.1	5.4	18.8
1.25	9.8	4.5	16.1
1.40	8.8	3.8	14.1
1.54	8.0	3.4	12.7
1.70	7.2	3.0	11.9
1.83	6.6	2.7	10.7
1.98	6.0	2.4	9.1
2.13	5.5	2.2	8.1
2.28	5.0	2.0	6.6
2.42	4.6	1.9	5.7
2.53	4.3	1.7	6.0

the factor of 2 for the perpendicular component into account, are summarized in Tables 5 and 6, respectively. The assumption that the distribution of the discrete oscillator strength is very low cannot be applied to the molecular case; therefore, our results are compared with experimental total photoabsorption as well as photoionization cross sections in Fig. 3 and Fig. 4.

Since we focus on the assessment of a new inversion method, we again compare with Veseth's results [13,14]. Several other results with different theoretical approaches are available for the computation of photoionization cross sections for N_2 [30,31] and CO [32,33].

The curves generated by polynomial inversion of the potential transform show a very good agreement with the experimental data for both molecules: the description of the absorption threshold is quite satisfactory for both molecules and the maximum of both curves is in a good accordance with the photoionization thresholds, similar to the observations made for the atomic results. At lower photon energies, both

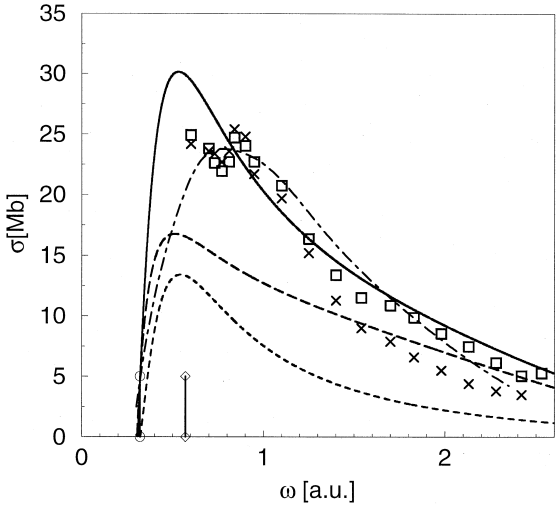


Fig. 3. Total photoionization (photoabsorption) cross section for N_2; results by polynomial inversion of the potential transform: $\sigma(\omega)$ (solid line), $\sigma(\omega)^{\perp}$ (long dashed line) and $\sigma(\omega)^{\parallel}$ (dashed line); results with Veseth's ansatz (Section 2.2.1) [12] (dot-dashed line); experimental results [35]: total photoabsorption (□) and photoionization (×) cross section. The first vertical line (○–○) indicates the energy of the first excited state $A^1\Pi_g$ at $\omega=0.321$ a.u., the second one (◇–◇) marks the photoionization threshold at $\omega=0.57$ a.u..

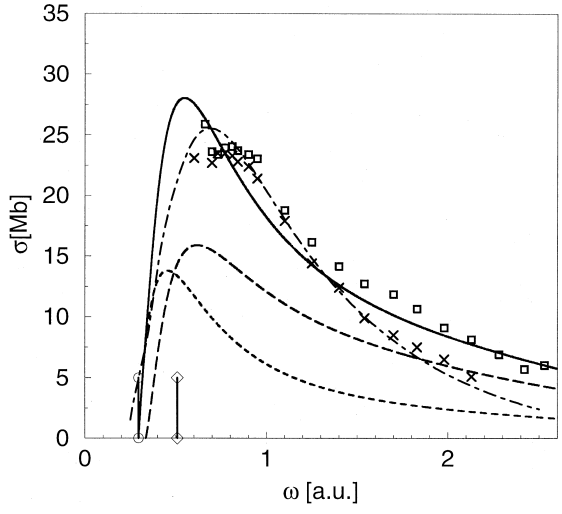


Fig. 4. Total photoionization (photoabsorption) cross section for CO; results by polynomial inversion of the potential transform: $\sigma(\omega)$ (solid line), $\sigma(\omega)^{\perp}$ (long dashed line) and $\sigma(\omega)^{\parallel}$ (dashed line); results with Veseth's ansatz (Section 2.2.1) [14] (dot-dashed line); experimental results [35]: total photoabsorption (□) and photoionization (×) cross section. The first vertical line (○–○) indicates the energy of the first excited state $A^1\Pi$ at $\omega=0.296$ a.u., the second one (◇–◇) marks the photoionization threshold at $\omega=0.51$ a.u..

experimental cross sections are quite similar in shape and magnitude. Around $\omega \approx 1.2$ a.u., the photoionization cross sections decrease faster with ω than the photoabsorption cross sections. Our results are very close to the photoabsorption cross section.

For lower photon energies both cross sections are characterized by a prominent structure due to excitations from particular shells. Veseth is considering these excitations by calculating the corresponding partial as well as the total cross section; in order to compare to our results, Figs. 3 and 4, we show only the total cross sections. For both N_2 and CO they are in reasonable agreement with the experimental data, but due to shortcomings of the exponential ansatz function, the cross sections are decreasing too fast with ω.

4. Summary and conclusions

We have discussed two methods for the inversion of dispersion integrals as needed for the evaluation of photoabsorption and photoionization cross sections of atoms and molecules. The first one is based on an 'analytic inversion' similar the one proposed by Veseth [11], but now applied to pairs of functions related by a Stieljes transform. This method has to rely on a certain ansatz function and, correspondingly, on a non-linear fit. The second one is a 'numerical inversion', which is realized in terms of the so-called 'potential' transform.

Both methods have been studied in applications to atomic and molecular systems. The inversion of the potential transform by polynomial approximation as discussed in Section 2.2.3 was found to yield satisfactory photoabsorption cross sections over the whole range of ω values considered, in contrast to earlier methods. This shortcoming of the 'analytic' inversion procedures, namely the inability of reproducing the cross section over the physically relevant frequency region, is due to an ansatz function with a fixed functional form. In addition, the necessity of a non-linear fit makes it quite difficult to reliably extrapolate the results beyond the experimentally measured domain.

As demonstrated for the atoms Ar and Kr as well as for the molecules N_2 and CO, one can improve on these problems by using an inversion procedure based on a linear fit to a polynomial according to Eqs. (16) and (17). The results obtained with this inversion method agree very well with the experimental atomic photoionization cross sections as well as with the experimental data for molecular photoabsorption. In particular, the locations of the physically relevant thresholds as well as the shape of the entire photoabsorption cross section are well reproduced. A crucial point is that these results are calculated *without* any non-linear fit procedure, which entails that the numerical inversion algorithm is associated with appreciable predictive power.

At this point, the description of the pronounced structures in molecular photoabsorption cross sections cannot be accomplished with our method. As discussed in Veseth's work, the reproduction of narrow resonances is a crucial issue even when considering partial cross sections. In order to accomplish this goal, the effects of molecular vibrations has to be taken into account as well as 'orbital resolved' (i.e., partial) cross sections. We plan to analyse the latter in terms of our inversion method as well, combined with the TDMP2-approach to extract the corresponding dynamic polarizabilities in a future work.

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