

Interference effects in H₂ photoionization at high energies

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Abstract

We present a theoretical study of H₂ ionization by photons of a few hundreds of eV. Accurate bound and continuum states are obtained by using *B*-spline basis functions. In agreement with a simple model by Cohen and Fano [6], we observe interference effects that can be interpreted as a result of the coherent emission from both molecular centres. Nevertheless, significant discrepancies are found at low electron energies, in agreement with recent experimental observations. The origin of this ‘anomalous’ behaviour at low electron energies is discussed in detail.

(Some figures in this article are in colour only in the electronic version)

Photoionization of the H₂ molecule has been extensively studied in the past (see [1] for a review). This is not surprising since hydrogen is the simplest neutral molecule and is the starting point to understand more complicated molecular systems. Previous investigations have focused on the region of low photon energies, where ionization is dominant and contribution from different doubly excited states is expected. In this work we present a theoretical study of H₂ photoionization at high photon energies, typically a few hundreds of eV. Very often, total cross sections in this energy region are available through analytical fits of experimental data obtained at lower photon energies [2, 3]. However, apart from simple models (see for instance [4]), accurate theoretical calculations in this energy region are very scarce [5].

Despite the lack of systematic investigations at high photon energies, Cohen and Fano [6] predicted long time ago that the spectrum of photoelectrons emerging from diatomic molecules is modulated by interferences. According to this, interference patterns coming from the coherent emission from both molecular centres should be observed at high photon impact energies. This prediction is based on three basic assumptions: (i) ionization is basically a *one*-electron process, (ii) the lowest molecular orbital ψ_g is well described in the LCAO⁴ approximation ($\psi_g \sim 1s_A + 1s_B$, where $1s_A$ and $1s_B$ are atomic orbitals centred in nucleus

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⁴ Linear combination of atomic orbitals.

A and B , respectively) and (iii) the ionized electron is well described by a single-centre plane wave. Using these simple ingredients, Cohen and Fano showed that the total photoionization cross section is given by the analytical form

$$\sigma = \sigma_H [1 + \sin(k_e R)/(k_e R)]/(1 + S) \quad (1)$$

where σ_H is the photoionization cross section of a hydrogen atom with effective charge Z_{eff} , R is the equilibrium internuclear distance, S is the overlap between $1s_A$ and $1s_B$, and k_e is the electron wave vector. This formula shows the typical oscillatory behaviour associated with interferences.

To our knowledge, these interferences have not been observed in photoionization experiments on H_2 . However, recent experiments [7] on single ionization of H_2 molecules by impact of fast heavy ions have shown interference patterns similar to those predicted by Cohen and Fano [6]. The latter observations have been supported by effective one-electron continuum distorted wave calculations [8] in which the initial molecular orbital is described as in the above model (i.e. as a combination of two $1s$ atomic orbitals). Analogous interference patterns have been predicted for electron impact on H_2 molecules using a similar description of the initial molecular orbital [9]. Although the general trends observed in the experiments are correctly described by these simple models, elaborate molecular wavefunctions are needed in order to explain the remaining discrepancies. In particular, the fact that, while equation (1) and the above theoretical models predict that the σ/σ_H ratio increases when k_e goes to zero, the experiments lead to the opposite conclusion.

An important issue is to quantify the validity of the three basic assumptions that support the predictions of the Cohen–Fano model and extensions of the latter. The key point is to obtain a realistic description of the true molecular states, including electron correlation and the strong oscillatory behaviour of the final two-centre continuum. Since this is a very difficult task for electron or ion impact, it seems appropriate to investigate in full detail the original problem, i.e. photoionization of H_2 .

To this end, we have applied the theoretical methods developed by Sánchez and Martín [10] to describe the molecular states of H_2 in a basis of B -splines [11]. These methods have been shown to provide an accurate representation of both bound and continuum states of H_2 , including correlation effects and the molecular character of the corresponding wavefunctions [1]. In the present application, the calculated cross sections extend up to photon energies of ~ 550 eV and are compared in detail with predictions of the Cohen–Fano model. Thus, the present results are useful to check the validity of this model and to test sources of energetic photons in the near future.

As we are not interested in the vibrational analysis of the residual H_2^+ ion, we will work in the fixed nuclei approximation [10], i.e. we will completely neglect the nuclear degrees of freedom. As explained in previous works [1, 11], this is a reasonable approximation for total cross sections, except very close to the ionization threshold and in the vicinity of the doubly excited states. This is because ionization is much faster than the typical vibrational or rotational periods of the molecule (except for the two cases just mentioned). We use the dipole approximation, average among all possible molecular orientations and sum over all possible final vibrational states. Thus, the total photoionization cross section (TPCS) is given by

$$\sigma(\omega) = \frac{4\pi^2\omega}{3c} \sum_{\alpha l_\alpha m_\alpha} \sum_p |\langle \Psi_g | \mathbf{e}_p \cdot \mathbf{D} | \Psi_{\alpha l_\alpha m_\alpha E}^+ \rangle|^2 \quad (2)$$

where ω is the photon energy, c is the speed of light, \mathbf{e}_p is the polarization vector along the p direction, \mathbf{D} is the dipole operator (in its length or velocity form), Ψ_g is the initial ground state of H_2 at the equilibrium distance $R = 1.4$ au (with energy E_g), and $\Psi_{\alpha l_\alpha m_\alpha E}^+$ is the final continuum

state of H₂ at $R = 1.4$ au with the usual outgoing boundary conditions, α is the electronic state of the residual H₂⁺ ion, l_α is the angular momentum of the ejected electron, m_α its projection along the molecular axis and $E = \hbar\omega + E_g$. Since the ground state of H₂ has $^1\Sigma_g^+$ symmetry, the dipole selection rule implies that only continuum states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetries can be populated. The wavefunctions have been evaluated as described in detail in [1, 10]. Briefly, the ground state Ψ_g results from a configuration interaction (CI) calculation in which the H₂ Hamiltonian has been diagonalized in a basis of 321 configurations built from products of one-electron molecular orbitals and pseudo-orbitals. The calculated energy is $-1.886\,5023$ au, to be compared with the exact non relativistic value $-1.888\,761\,38$ au [12]. The final continuum state $\Psi_{\alpha l_\alpha m_\alpha E}^+$ results from a close coupling calculation that includes open channels associated with the four lowest ionization thresholds of H₂: $X^2\Sigma_g^+(1s\sigma_g)$, $^2\Sigma_u^+(2p\sigma_u)$, $^2\Pi_u(2p\pi_u)$ and $^2\Sigma_g^+(2s\sigma_g)$. Therefore, both wavefunctions include electron correlation and the two-centre character of the molecular potential. In addition, $\Psi_{\alpha l_\alpha m_\alpha E}^+$ accounts for interferences among the various ionization thresholds and angular momenta of the ejected electron. To check the convergence of the close coupling expansion, we have performed additional calculations (for a reduced number of photon energies) in which six additional ionization thresholds have been included.

The one-electron basis functions are written as $r^{-1}B_i^k(r)Y_l^m(\hat{r})$, where $Y_l^m(\hat{r})$ is a spherical harmonic and B_i^k is the i th B -spline of order k (polynomial of degree $k - 1$) defined in the interval $[0, r_{\max}]$ [11]. The knot sequence has been chosen so that $B_i^k(0) = B_i^k(r_{\max}) = 0$. The orbitals of H₂⁺, or target states, are obtained by diagonalization of the corresponding one-electron Hamiltonian in the above basis, so that they are written as

$$\varphi_{nm} = \sum_{l=0}^{l_{\max}} \sum_{i=0}^{N_l} c_{il}^n \frac{B_i^k(r)}{r} Y_l^m(\hat{r}). \quad (3)$$

In this work we have used $k = 8$, $r_{\max} = 60$ au, $N_l = 280$ and a linear knot sequence. We have included angular momenta up to $l_{\max} = 11$. Since we have 280 B -spline functions per angular momentum, σ_g orbitals are expansions of 1680 terms ($l = 0, 2, 4, 6, 8$, and 10), σ_u orbitals of 1680 terms ($l = 1, 3, 5, 7, 9$ and 11), π_g orbitals of 1400 terms ($l = 2, 4, 6, 8$, and 10), and so on. It must be noticed that, for each l , the number of B -splines N_l is substantially larger than in previous calculations of H₂ photoionization. This is due to the strong oscillatory behaviour of the final continuum states at the high photon energies considered in this work. Indeed, converged results can only be obtained when each wavelength contains at least $N_\lambda = 3$ knotpoints [11], which leads to a minimum number of $N_{l,\min} = N_\lambda r_{\max} k_e / \pi$ B -splines for an electron energy of $k_e^2/2$ (e.g., $N_{l,\min} \simeq 280$ for $k_e = 5$ au). We have checked the accuracy of the B -spline basis set in the case of the H₂⁺ molecular ion. For this molecular ion, our calculated TPCS is in good agreement with converged results obtained by Brosolo *et al* [13].

In the case of H₂, a comparison between 4-channel and 10-channel calculations shows that the calculated TPCS is practically converged in the velocity gauge for all photon energies considered in this work. This is not the case in the length gauge, especially at high photon energies where the TPCS is extremely small and comparable to the difference between the 4-channel and 10-channel calculations. For this reason, only results obtained in the velocity gauge will be shown below. Figure 1 shows the TPCS of H₂ as a function of photon energy up to 20 au. The cross section decreases by many orders of magnitude as the photon energy increases. The present results agree well with the experimental measurements of Samson and Haddad [2] at low photon energies. They agree reasonably well with recent extrapolations of the TPCS at higher photon energies reported by Yan *et al* [3] and Samson and Haddad [2]. In the latter case, the agreement worsens as the photon energy increases. None of these fits goes

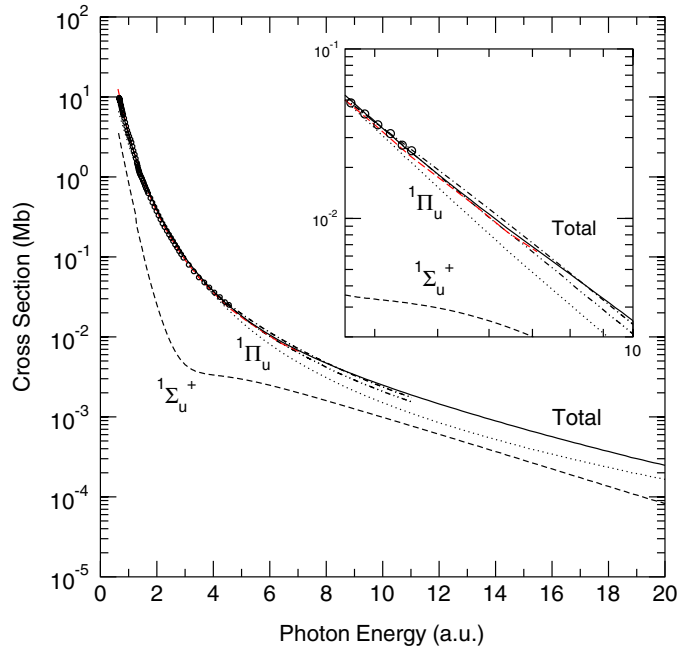


Figure 1. Total photoionization cross section of H_2 as a function of photon energy. Full line, total cross section. Short dashed line, $^1\Sigma_u^+$ contribution. Dotted line, $^1\Pi_u$ contribution. Circles, experimental results of Samson and Haddad taken from [14]. Dashed and double dotted line, fit of the latter experimental results at higher photon energies [2]. Dashed and dotted line, fit by Yan *et al* [3]. Long dashed line (red curve in the electronic version of the paper), RPA results [5].

beyond 11 au. Our calculated TPCS is also in good agreement with recent theoretical results obtained in the random phase approximation (RPA) [5] up to 7 au. Figure 1 also shows the contribution of the $^1\Sigma_u^+$ and $^1\Pi_u$ final symmetries. It can be seen that the $^1\Pi_u$ contribution decreases monotonically with photon energy and that it is the dominant contribution to the TPCS. The $^1\Sigma_u^+$ contribution exhibits a pronounced non-monotonous behaviour. This is barely apparent in the TPCS shown in figure 1 due to the dominant contribution of the $^1\Pi_u$ symmetry.

Figure 2 shows the contribution of the different ionization thresholds to the $^1\Sigma_u^+$ cross section. As can be seen, the $X^2\Sigma_g^+(1s\sigma_g)$ threshold leads to the dominant contribution. Its behaviour as a function of photon energy is practically identical to that of the total $^1\Sigma_u^+$ cross section. We have obtained a similar conclusion for the $^1\Pi_u$ cross section. This leads us to conclude that the oscillatory behaviour observed in figure 2 is mainly due to ionization of one of the electrons without excitation of the other, which supports the validity of the one-electron picture used in the Cohen–Fano model. Nevertheless, as figure 2 shows, the oscillations are slightly less pronounced in the total cross section than in the $X^2\Sigma_g^+(1s\sigma_g)$ partial cross section.

In figure 3, we show the contribution of the individual $\Psi_{\alpha l_\alpha m_\alpha E}^+$ channels to the $X^2\Sigma_g^+(1s\sigma_g)$ cross section of $^1\Sigma_u^+$ symmetry. As can be seen, the $l_\alpha = 1$ channel dominates at low and high photon energies. The $l_\alpha = 3$ channel is dominant between 2.46 and 6.57 au and the $l_\alpha = 1$ channel practically vanishes at about 3.36 au. This behaviour is in contrast with that of the Cohen–Fano model [6] that predicts that the $l = 1$ cross section is never dominant beyond $\simeq 3$ au. Our results are much closer to those obtained in the RPA calculations of [5]. Nevertheless, the position of the $l = 1$ minimum in the latter calculations appears at around 3.0 au, which is slightly lower than ours.

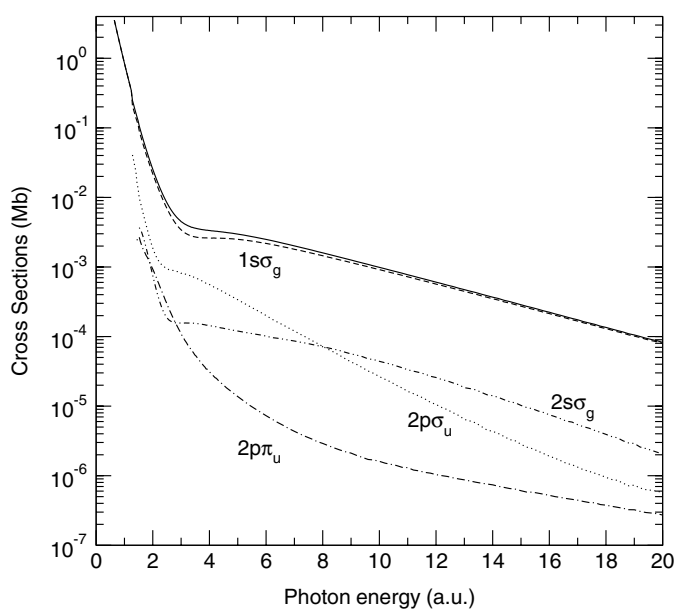


Figure 2. Contribution of different ionization thresholds to the $^1\Sigma_u^+$ photoionization cross section of H₂. Full line, $^1\Sigma_u^+$ cross section; dashed line, $X^2\Sigma_g^+(1\sigma_g)$; dotted line, $^2\Sigma_u^+(2p\sigma_u)$; dashed and dotted line, $^2\Pi_u(2p\pi_u)$; double dashed and dotted line, $^2\Sigma_g^+(2s\sigma_g)$.

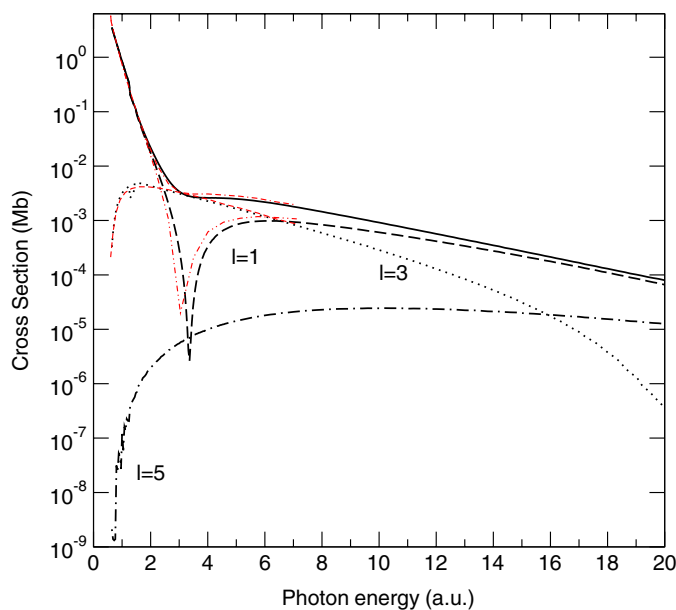


Figure 3. Contribution of different partial waves to the $^1\Sigma_u^+(1\sigma_g)$ photoionization cross section of H₂. Present results: full line, $^1\Sigma_u^+$ cross section; long dashed line, $l=1$; dotted line, $l=3$; dashed and dotted line, $l=5$. Results of Semenov and Cherepkov [5] (red curves in the electronic version of the paper): double dashed dotted line, $^1\Sigma_u^+$ cross section; dashed double dotted line, $l=1$; short dashed line, $l=3$.

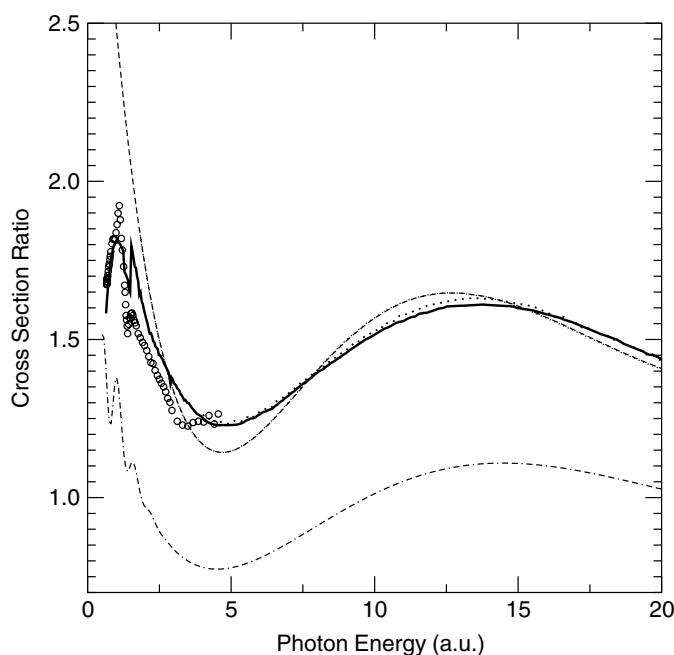


Figure 4. The $\sigma_{\text{H}_2}/2\sigma_{\text{H}}$ photoionization ratio. Full line, 4-channel *ab initio* results; dotted line, 10-channel *ab initio* results; circles, experimental results of Samson and Haddad taken from [14] and divided by $2\sigma_{\text{H}}$; dashed line, fit of $\sigma_{\text{H}_2}/2\sigma_{\text{H}}$ to the Cohen–Fano formula (1) (see text); dashed and dotted line, results for a fictitious one electron molecule with nuclear charges equal to 0.5; for the sake of clarity, the resulting curve has been multiplied by 0.25 (see text for details).

To analyse the validity of equation (1), we have divided the calculated TPCS of H_2 by twice the TPCS of atomic H. The result is shown in figure 4 as a function of photon energy. Strong oscillations are now clearly visible. These oscillations are also present in the 10-channel calculation. Very often, oscillations as those predicted by equation (1) are interpreted as the result of the coherent superposition of electronic waves arising from each molecular centre. This qualitative picture is compatible with the fact that oscillations are only observed in the $^1\Sigma_u^+$ symmetry: $^1\Pi_u$ states have a nodal plane containing both nuclei and, consequently, the possibility of a coherent sum of amplitudes is substantially reduced. To better understand the physical origin of the oscillations shown in figure 4, we have fitted the calculated curve to the Cohen–Fano formula (1), leaving $a_0 = \sigma_{\text{H}}/(1 + S)$ and $a_1 = R$ as free parameters. The result of the fit ($a_0 = 1.46$ and $a_1 = 1.57$) is shown in figure 4. The good quality of the fit at high photon energies supports the physical image of the Cohen–Fano model. Nevertheless, the fact that a_1 is slightly different from the value of the equilibrium distance ($R = 1.4$ au) raises some doubts about its quantitative value. Extensions of this model have been proposed to interpret similar oscillatory behaviours observed in ionization of D_2 by fast heavy ions [7] and electrons [15]. As in the Cohen–Fano model [6], these theories are based on a one-electron description of ionization and an LCAO representation of the initial molecular state. This has led to results in reasonable agreement with experiments for large k_e . However, as mentioned above, none of these theories has been able to reproduce the fall of the experimental $\sigma/2\sigma_{\text{H}}$ ratio when k_e decreases (see figure 4). The present results do show such a fall, in excellent agreement with the measurements of Samson and Haddad [2] (see figure 4). This is the first theoretical evidence of these observations.

The failure to reproduce the observed behaviour at relatively low photon energies using the fitting function given in equation (1) indicates that at least one of the basic assumptions of the Cohen–Fano model does not hold. To get a deeper insight into this problem, we show in figure 4 the results of a *B*-spline calculation for a *fictitious* one-electron diatomic molecule with nuclear charges $Z = 0.5$ and equilibrium distance $R = 1.4$ au. This system differs from the real H₂ molecule in the absence of correlation and screening. All the other aspects are treated as in H₂: exact molecular description of both the initial and final states, close-coupling description of continuum states, same *B*-spline basis, etc. It can be seen that the results of this model calculation reproduce qualitatively those of H₂ at high electron energies. However, at lower energies, the model fails to reproduce the fall of the $\sigma/2\sigma_{\text{H}}$ ratio. Therefore, the origin of this fall must be electron correlation and/or screening. Indeed, at low k_e , the ejected electron is more sensitive to details of the potential near the nuclei. In particular, in a real H₂ molecule, a slow electron feels a charge larger than 0.5 due to incomplete screening of the inner electron, which must lead to a decrease of the ionization cross section. Electron correlation is expected to play a significant role only in the vicinity of the doubly excited states of H₂, where the nuclear motion cannot be neglected. Figure 4 shows some structure near the ionization threshold on the curve of the fictitious one-electron molecule. This is likely due to the two-centre character of the electronic continuum, which is absent in the Cohen–Fano model, but must be visible for electrons with small kinetic energy.

In summary, total photoionization cross sections of H₂ have been evaluated at high photon energies using a *B*-spline approach that allows one to accurately describe electron correlation and the true molecular character of the H₂ electronic states. Our findings support the existence of interference patterns as those predicted by Cohen and Fano resulting from the coherent emission of both molecular centres. We have explained the behaviour observed in previous experiments at relatively low electron energies as the result of incomplete screening and/or electron correlation. These two effects are not accounted for by the Cohen–Fano model. A possible extension of this work is to consider the nuclear degrees of freedom. Although the above conclusions will certainly remain unchanged because they only concern total cross sections, it will be possible to analyse, e.g., the final vibrational distribution of the remaining H₂⁺ ions. Work along this line is now in progress in our laboratory.

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References

- [1] Martín F 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** R197
- [2] Samson J A R and Haddad G N 1994 *J. Opt. Soc. Am. B* **11** 277
- [3] Yan M, Sadeghpour H R and Dalgarno A 1998 *Astrophys. J.* **496** 1044
- [4] Walter M and Briggs J 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** 2487
- [5] Semenov S K and N A Cherepkov 2003 *J. Phys. B: At. Mol. Opt. Phys.* **36** 1409
- [6] Cohen H D and Fano U 1966 *Phys. Rev.* **150** 30
- [7] Stolterfoht *et al* 2001 *Phys. Rev. Lett.* **87** 023201

-
- [8] Galassi M E, Rivarola R D, Fainstein P D and Stolterfoht N 2002 *Phys. Rev. A* **66** 052705
 - [9] Stia C R, Fojon O A, Weck P F, Hanssen J and Rivarola R D 2003 *J. Phys. B: At. Mol. Opt. Phys.* **36** L1
 - [10] Sánchez I and Martín F 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 679
 - [11] Bachau H, Cormier E, Decleva P, Hansen J E and Martín F 2001 *Rep. Prog. Phys.* **64** 1815
 - [12] Kolos W, Szalewicz K and Monkhorst H J 1986 *J. Chem. Phys.* **84** 3278
 - [13] Brosolo M, Decleva P and Lisini A 1999 *Chem. Phys.* **181** 85
 - [14] Chung Y M, Lee E M, Masuoka T and Samson J A R 1993 *J. Chem. Phys.* **99** 885
 - [15] Frémont F *et al* 2003 *Proc. XXIII ICPEAC (Stockholm, Sweden)* Fr062