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Theoretical study of vibrationally resolved photoionization for the C K-shell of the CO molecule

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Abstract

Partial photoionization cross sections and the angular asymmetry parameter β for the C K-shell of the CO molecule have been calculated in the relaxed core Hartree–Fock approximation. In contrast with all previous calculations, we introduced the relaxed core potential with a fractional charge of the ion which was fitted from the condition to get an agreement with the experimental position of the σ^* shape resonance for the K-shell cross section. We found the optimal value of the fractional charge to be 0.5. After performing calculations within the Born–Oppenheimer approximation for several fixed internuclear distances R, we averaged the R-dependent dipole amplitudes over R with the vibrational wavefunctions of the initial and final states. Transitions from the ground vibrational level to several vibrationally excited states of the residual molecular ion have been studied within this approximation. A good agreement was found with the recently published vibrationally resolved experimental data.

1. Introduction

In the majority of theoretical considerations the molecular photoionization process is studied in the Born–Oppenheimer approximation at a fixed internuclear distance. On the other hand, it was shown theoretically rather long ago by Dehmer *et al* [1] and Raseev *et al* [2] in the example of the N_2 molecule that the position and strength of the σ^* shape resonance are sensitive functions of the nuclear separation R. In other words, the nuclear motion is influencing the photoionization process, especially in the vicinity of the shape resonances. To take it into account, it was proposed in [1] to perform calculations for several fixed internuclear distances R and then to average the R-dependent dipole amplitudes $d(\omega, R)$ over R weighted with the product of the vibrational wavefunctions $\chi_v(R)$ of the initial and final states. At that time, the difference between theory and experiment for the K-shell cross section was frequently about a factor of 2 [3], while the influence of vibrational motion was substantially smaller. As a result, in the following investigations the vibrational averaging was not performed.

In the recent more advanced calculations [4–12] it became possible to get much closer agreement with experiment, so that the contribution of vibrational motion to the cross section can now be comparable to the difference between theory and experiment. Moreover, due to substantial progress in experimental technique, it became possible to measure the vibrationally resolved partial cross sections and the angular asymmetry parameter β for the particular case of photoionization of the C K-shell of the CO molecule [13]. It was shown there that with increasing of the final state vibrational quantum number v' the maximum of the σ^* shape resonance in the corresponding partial cross section moves substantially to lower energies. The goal of this study is to check the applicability of a recently developed version of the relaxed core Hartree–Fock approximation [10, 11] to describe these data. The preliminary results of this study have been published in [14]. We are not aware of any calculation of the vibrationally resolved angular asymmetry parameter β for this case. The vibrationally resolved cross sections for C and O K-shells of the CO molecule have been calculated earlier within a relatively simple quasi-atomic model [15]. Our study was further motivated by the appearance of the most sophisticated experimental data on vibrationally resolved molecule frame photoelectron angular distributions [14] which is the next step in getting a deeper insight into the influence of vibrational motion on the photoionization process.

2. Theoretical approach

2.1. Fractional charge relaxed core Hartree–Fock approximation

Our calculations in this paper are restricted by the Hartree–Fock (HF) approximation. We checked numerically using our RPA programme for the equilibrium internuclear distance ($R = 2.132$ au) that the contribution of both intra- and inter-shell RPA correlations is insignificant and does not exceed 3%. This is because the intrashell RPA correlations are usually small for two-electron subshells and in particular for K-shells. As to the intershell correlations, they give a substantial contribution in the case of K-shells of the N_2 molecule [11] due to a very small difference in energy (about 0.1 eV) between the $1\sigma_g$ and $1\sigma_u$ shells, while the C K-shell of the CO molecule is separated in energy by about 200 eV from both the O K-shell and the valence shells. Due to that the intershell RPA correlations for the C K-shell of the CO molecule are negligible, too. The other kinds of many-electron correlations describing the relaxation of the molecular wavefunctions after creation of a deep hole in the K-shell (which are beyond the RPA approximation) are really important, and they are taken into account by using the relaxed core HF approximation.

The Hartree–Fock ground-state wavefunctions of a diatomic molecule are the solutions of the system of self-consistent equations

$$\left[-\frac{\nabla^2}{2} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \sum_{j=1}^{n} a_{ij} J_{jj}(\mathbf{r})\right] \varphi_i(\mathbf{r}) - \sum_{j=1}^{n} b_{ij} J_{ji}(\mathbf{r})\varphi_j(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) + \sum_{j=1}^{n} \varepsilon_{ij}\varphi_j(\mathbf{r}), \tag{1}$$

where n is the number of occupied orbitals, $i \leqslant n$, ε_i is the energy of the orbital and $J_{ji}(r)$ are defined as

$$J_{ji}(\mathbf{r}) = \int \varphi_j^*(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-1}\varphi_i(\mathbf{r}')\,\mathrm{d}\mathbf{r}'. \tag{2}$$

They describe the exchange interaction when $i \neq j$ and the direct interaction when $i = j$. The values of off-diagonal energy parameters ε_{ij} are determined from the orthogonalization condition

$$\int \varphi_j^*(\mathbf{r})\varphi_i(\mathbf{r})\,\mathrm{d}\mathbf{r} = 0. \tag{3}$$

In the case of a closed shells molecule the parameters of equation (1) are

$$a_{ij} = 2, \qquad b_{ij} = 1, \qquad \varepsilon_{ij} = 0. \tag{4}$$

For an excited state wavefunction φ_f in the field of a singly charged ion, the equation in a frozen core HF (FCHF) approximation is similar to (1)

$$\left[-\frac{\nabla^2}{2} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \sum_{j=1}^{n} a_{fj} J_{jj}(\mathbf{r})\right]\varphi_f(\mathbf{r}) - \sum_{j=1}^{n} b_{fj} J_{jf}(\mathbf{r})\varphi_j(\mathbf{r}) = \varepsilon_f \varphi_f(\mathbf{r}) + \sum_{j=1}^{n} \varepsilon_{fj}\varphi_j(\mathbf{r}), \tag{5}$$

where $f > n$,

$$\begin{aligned} &a_{fj} = 2, \qquad b_{fj} = 1, \qquad j \neq i', \\ &a_{fi'} = 1, \qquad b_{fi'} = -1. \end{aligned} \tag{6}$$

The index i' corresponds to the ionized shell. The off-diagonal energy parameters provide the orthogonalization of the excited state wavefunction to the ground-state (core) wavefunctions

$$\int \varphi_i^*(\mathbf{r})\varphi_f(\mathbf{r})\,\mathrm{d}\mathbf{r} = 0. \tag{7}$$

It is well known that in the case of ionization of molecular K-shells, the effect of core relaxation after ejection of one electron must be taken into account [16]. It is usually done in the framework of the relaxed core HF (RCHF) approximation implying that the excited state wavefunctions satisfy equation (5) with the potential calculated with another set of wavefunctions. Namely, the new set of the self-consistent bound state wavefunctions of the molecular ion is calculated with one electron absent from the (two-electron) i' shell. It is achieved by solving equation (1) with the coefficients given below

$$\begin{aligned} &a_{i'i'} = b_{i'i'} = 0, \qquad a_{ii'} = 1, \qquad b_{ii'} = 0.5, \qquad i \neq i', \\ &a_{ij} = 2, \qquad b_{ij} = 1, \qquad i \neq i'. \end{aligned} \tag{8}$$

Here the first line means that the HF interaction is absent in the one-electron ionized shell, and the HF interaction of the ionized shell with all others becomes two times smaller. The second line shows that the other parts of the HF interaction are not changed. The parameters $\varepsilon_{ij} \neq 0$ and should be calculated from condition (3).

On the other hand, it is also known that the RCHF method overestimates the influence of the relaxation effects for K-shells [16]. Therefore, we propose here the fractional charge RCHF method which corresponds to some intermediate value of the charge of the hole state. To this end, we calculate the relaxed core wavefunctions $\varphi_f^R(\mathbf{r})$ as solutions of equation (1) with the coefficients lying between those given by equations (4) and (8). Namely, the coefficients are expressed through the fractional parameter z_e ($0 < z_e < 1$) by the equations

$$\begin{aligned} &a_{i'i'} = 2(1 - z_e), \qquad b_{i'i'} = 1 - z_e, \\ &a_{ii'} = 2 - z_e, \qquad b_{ii'} = 0.5(2 - z_e), \qquad i \neq i', \\ &a_{i'j} = 2, \qquad b_{i'j} = 1, \qquad j \neq i'. \end{aligned} \tag{9}$$

We consider z_e as a free parameter which is found from the condition to reproduce correctly the position of the σ^* shape resonance. The FCHF approximation corresponds to $z_e = 0$, while the standard RCHF method with the integer charge corresponds to $z_e = 1$. The orthogonalization conditions

$$\int \varphi_i^{R*}(\mathbf{r})\varphi_{i'}^R(\mathbf{r})\,\mathrm{d}\mathbf{r} = 0 \tag{10}$$

are fulfilled by introducing the non-diagonal energy parameters $\varepsilon_{i'j}$, $\varepsilon_{ji'}$ as

$$\varepsilon_{i'j} = 2\varepsilon_{ji'} = z_e \int\int \varphi_{i'}^{R*}(\mathbf{r})\varphi_{i'}^R(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\varphi_{i'}^R(\mathbf{r}')\varphi_j^{R*}(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}', \tag{11}$$

or in a symbolic form

$$\varepsilon_{i'j} = 2\varepsilon_{ji'} = z_e\langle\varphi_{i'}^R, \varphi_j^R\big|U\big|\varphi_{i'}^R, \varphi_{i'}^R\rangle, \tag{12}$$

where U means the Coulomb potential.

After that the excited state wavefunctions of discrete and continuous spectra are found as solutions of equation (5) with the coefficients (6) and with the fractional charge relaxed core wavefunctions in the HF potential, while the orthogonalization conditions (7) are now transformed to

$$\begin{aligned}\varepsilon_{fi} = {} & \sum_{i=1}^{n} a_{ji}\langle\varphi_f, \varphi_i|U|\varphi_j, \varphi_i\rangle - \sum_{i=1}^{n} b_{ji}\langle\varphi_f, \varphi_i|U|\varphi_i, \varphi_j\rangle \\ & - \sum_{i=1}^{n} a_{fi}\langle\varphi_j, \varphi_i^R\big|U\big|\varphi_f, \varphi_i^R\rangle + \sum_{i=1}^{n} b_{fi}\langle\varphi_j, \varphi_i^R\big|U\big|\varphi_i^R, \varphi_f\rangle,\end{aligned} \tag{13}$$

where the coefficients a_{ji}, b_{ji} are taken from (4).

2.2. Calculations of the cross section and the angular distribution

Keeping in mind the further application for calculations of the angular distribution of photoelectrons, we determine photoionization parameters through the photoelectron orbital $\psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ with the incoming wave boundary condition. Here $\mathbf{k}$ is the electron momentum and $\mathbf{r}$ is its coordinate. The partial wave expansion of this orbital in the molecular frame is given as usual [17–19] by

$$\psi_{\mathbf{k}}^{(-)}(\mathbf{r}) = \sum_{l,m} f_{\varepsilon lm}(\mathbf{r})Y_{lm}^*(\hat{\mathbf{k}}), \tag{14}$$

where $\varepsilon = k^2/2$ is the photoelectron energy, the functions $f_{\varepsilon lm}(\mathbf{r})$ satisfy equation (5) and have the asymptotic

$$f_{\varepsilon lm}(\mathbf{r})|_{r\to\infty} \sim \left(\frac{2}{\pi k}\right)^{1/2} \frac{1}{2\mathrm{i}r}\left(Y_{lm}(\hat{\mathbf{r}})\,\mathrm{e}^{\mathrm{i}\vartheta(r)} - \sum_{l'} Y_{l'm}(\hat{\mathbf{r}})S_{ll'm}^*\mathrm{e}^{-\mathrm{i}\vartheta(r)}\right) \tag{15}$$

with $\vartheta(r) = kr + k^{-1}\ln 2kr$. They are normalized to the energy δ-function. Within the Born–Oppenheimer approximation, the differential photoionization cross section in the length form can be written as (atomic units $\hbar = m = e = 1$ are used in this paper)

$$\mathrm{d}\sigma(\omega)/\mathrm{d}\Omega_k = 4\pi^2\alpha a_0^2\omega\sum_{\mu}|\langle\psi^{(-)}(\mathbf{k}, \mathbf{r})|d_\mu|0\rangle|^2, \tag{16}$$

where ω is the photon energy, Ω_k denotes the spherical angles of the vector $\mathbf{k}$, α is the fine-structure constant, a_0 is the Bohr radius, $|0\rangle$ means the initial (ground) state of the molecule and d_μ are the spherical projections of the dipole operator

$$d_\mu = \sqrt{\frac{4\pi}{3}}rY_{1\mu}(\hat{\mathbf{r}}). \tag{17}$$

The rotational motion is here neglected. From equation (16) one gets the usual expression for the angular distribution of photoelectrons (for unpolarized or circularly polarized light)

$$\mathrm{d}\sigma(\omega)/\mathrm{d}\Omega_k = \frac{\sigma(\omega)}{4\pi}\left[1 - \frac{\beta}{2}P_2(\cos\theta_k)\right], \tag{18}$$

where $\sigma(\omega)$ is the total photoionization cross section

$$\sigma(\omega) = \frac{4}{3}\pi^2\alpha a_0^2\omega B, \qquad B = \sum_{\mu}\sum_{l,m}|\langle f_{\varepsilon lm}(\mathbf{r})|d_\mu|\mathrm{i}\rangle|^2, \tag{19}$$

while the asymmetry parameter β is defined by the equation

$$\begin{aligned}\beta = \frac{\sqrt{30}}{B}\sum_{l_1,l_2}\sum_{m_1,m_2}\sum_{M_L}(\mathrm{i})^{l_2-l_1}\exp\left[\mathrm{i}\left(\delta_{l_1m_1}-\delta_{l_2m_2}\right)\right]\sqrt{[l_1,l_2]}\\ \times\begin{pmatrix} l_1 & l_2 & 2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & l_2 & 2\\ m_1 & -m_2 & -M_L\end{pmatrix}\begin{pmatrix} 1 & 1 & 2\\ m_1 & -m_2 & -M_L\end{pmatrix}\\ \times\left\langle f_{\varepsilon l_1m_1}(\mathbf{r})\middle|d_{m_1}|0\right\rangle\langle 0|d^*_{m_2}\middle|f_{\varepsilon l_2m_2}(\mathbf{r})\right\rangle.\end{aligned} \tag{20}$$

The method of calculation of the continuum wavefunctions $f_{\varepsilon lm}(\mathbf{r})$ has been described earlier in [10, 20]. Namely, instead of the functions $f_{\varepsilon lm}(\mathbf{r})$ which include an imaginary part, the set of real functions $\varphi_{\varepsilon lm}(\mathbf{r})$ is calculated as the solution of the FCHF equation (5) satisfying the asymptotic relations

$$\varphi_{\varepsilon lm}(\mathbf{r})|_{r\to\infty} \sim \frac{1}{r}\left(\frac{2}{\pi k}\right)^{1/2}\sum_{l'}c^{\varepsilon m}_{ll'}Y_{l'm}(\hat{\mathbf{r}})\sin\left(\vartheta(r)+\delta^{\varepsilon m}_{ll'}\right), \qquad \sum_{l'}\left(c^{\varepsilon m}_{ll'}\right)^2 = 1, \tag{21}$$

and the orthonormalization conditions

$$\langle\varphi_{\varepsilon lm}|\varphi_{\varepsilon' l'm'}\rangle = \delta_{ll'}\delta_{mm'}\delta(\varepsilon-\varepsilon'). \tag{22}$$

The functions $\varphi_{\varepsilon lm}(\mathbf{r})$ are connected to the functions $f_{\varepsilon lm}(\mathbf{r})$ by the equation

$$\varphi_{\varepsilon lm}(\mathbf{r}) = \sum_{l'}c^{\varepsilon m}_{ll'}f_{\varepsilon l'm}(\mathbf{r})\exp\left(\mathrm{i}\delta^{\varepsilon m}_{ll'}\right), \tag{23}$$

or, since $c^{\varepsilon m}_{ll'}\exp\left(\mathrm{i}\delta^{\varepsilon m}_{ll'}\right)$ form a unitary matrix,

$$f_{\varepsilon lm}(\mathbf{r}) = \sum_{l'}c^{\varepsilon m}_{l'l}\varphi_{\varepsilon l'm}(\mathbf{r})\exp\left(-\mathrm{i}\delta^{\varepsilon m}_{l'l}\right). \tag{24}$$

Inserting this equation into equations (19), (20), we express the photoionization parameters σ, β through the set of calculated wavefunctions $\varphi_{\varepsilon lm}(\mathbf{r})$.

We are presenting in this paper only the results obtained in the length form, though the calculations have been performed also in the velocity form. The difference between the length and velocity cross sections is about 3–4% for RCHF and less then 2% for RCHF (0.5) provided the experimental ionization threshold 296.2 eV is used (theoretical threshold is at 303.1 eV), while the difference in β values is less then 1%. Therefore, it is sufficient to present the results only in one form.

2.3. Vibrationally resolved calculations

The calculations described above have been performed for several fixed internuclear distances R, giving a set of the dipole matrix elements $d_{lm}(\omega, R) = \langle f_{\varepsilon lm}(\mathbf{r})|d_m|\mathrm{i}\rangle$ for each photon energy ω. To obtain the matrix element for the vibrationally resolved transition, $d_{v'v}(\omega)$, the values $d_{lm}(\omega, R)$ were multiplied by the corresponding initial and final vibrational state

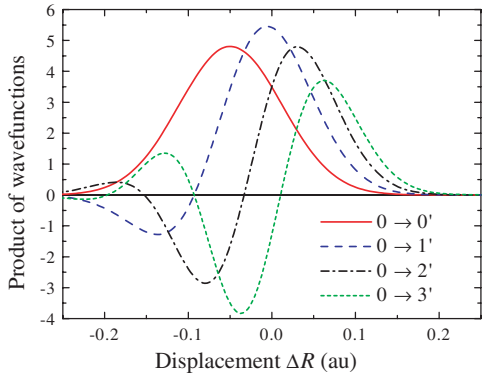

Figure 1. The products of the vibrational wavefunctions of the initial ($v = 0$) and final ($v' = 0, 1, 2, 3$) states which define the integrand in equation (25). The zero value of ΔR corresponds to the equilibrium internuclear distance $R = 2.132$ au.

wavefunctions, $\chi_v(R)$ and $\chi_{v'}(R)$, which are the harmonic oscillator wavefunctions, and integrated over the internuclear distance R

$$d_{v'v}(\omega) = \int \chi_{v'}(R) d_{lm}(\omega, R) \chi_v(R)\, \mathrm{d}R. \tag{25}$$

Assuming that in the initial state only the ground vibrational level $v = 0$ is populated, we integrated over R using 11 points around the equilibrium distance $R = 2.132$ au of the ground state [13] with the step 0.05 au. The equilibrium internuclear distance for the molecular ion state was taken from [13] to be 2.042 au. The vibrational spacings are 0.269 eV for the ground state and 0.302 eV for the ion state. To prove that the 11 points in R mentioned above are sufficient for obtaining the convergent result, we show in figure 1 the products of the vibrational wavefunctions entering equation (25) in that region of R. The matrix elements (25) have been substituted into equations (19), (20) to calculate the vibrationally resolved cross sections and the angular asymmetry parameter β.

We also made additional calculations in order to elucidate the role of averaging of the total cross section over the internuclear distance in the initial vibrational state $v = 0$. To take into account the nuclear motion in the initial state only, the partial photoionization cross sections $\sigma(\omega, R)$ calculated separately for several values of R are averaged over the internuclear distances using the equation

$$\sigma_{\mathrm{av}}(\omega) = \int \chi_v^2(R) \sigma(\omega, R)\, \mathrm{d}R, \tag{26}$$

where $\chi_v(R)$ is the vibrational wavefunction of the initial state. We checked that this cross section is only 1–3% higher than the sum of vibrationally resolved partial cross sections calculated with the matrix elements defined by equation (25), and therefore it is not shown in the paper.

3. Results of calculations

3.1. Vibrationally resolved partial cross sections

To decide which fractional charge z_e in equation (9) is more appropriate for the C K-shell, we performed calculations with three values of z_e equal to 1, 0.7 and 0.5. Figures 2 and 3 show the

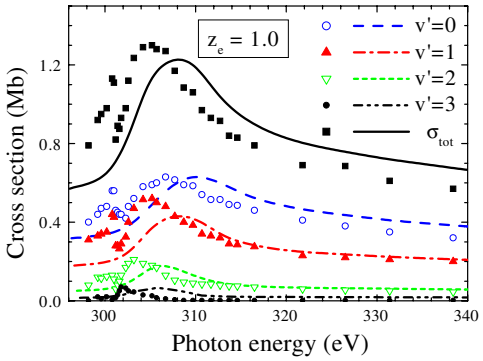

Figure 2. Partial photoionization cross sections for different vibrational transitions and the total cross section for ionization of the C K-shell of the CO molecule calculated in the RCHF approximation with the integer charge $z_e = 1.0$ (curves). The corresponding experimental data points are taken from [13].

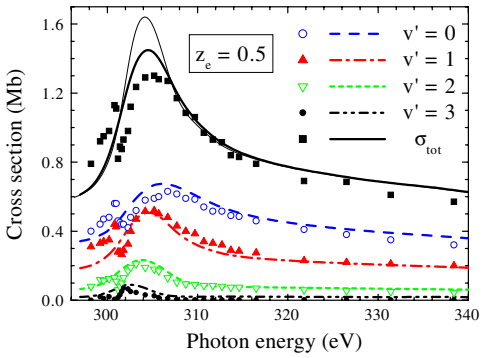

Figure 3. Partial photoionization cross sections for different vibrational transitions and the total cross section for ionization of the C K-shell of the CO molecule calculated in the RCHF (0.5) approximation with the fractional charge $z_e = 0.5$ (curves). Thin solid line shows the total cross section calculated for the (fixed) equilibrium internuclear distance. The corresponding experimental data points are taken from [13].

partial photoionization cross sections for different vibrational transitions and the total cross section (obtained as a sum of partial cross sections) calculated in the RCHF approximation with the charges z_e= 1.0 and 0.5, respectively (the latter will be denoted below as RCHF (0.5)). They are compared with the corresponding experimental data of Köppe *et al* [13]. The results of the RCHF calculation shifted by 2 eV to lower energies were presented earlier in [14]. The fractional charge $z_e = 0.5$ was selected from the condition to get a better agreement with the experimental position of the maximum of the σ^* shape resonance in the partial and total cross sections. The similar RCHF calculation with the integer charge $z_e = 1.0$ (denoted below as RCHF) shown in figure 2 gives the position of the maximum in the total cross section at 308 eV photon energy, that is about 3 eV higher than in the experiment. On the other hand, in RCHF (0.5) it is slightly lower than in the experiment. While in the RCHF the maximum of the σ^* shape resonance is lower than in the experiment, in RCHF (0.5) it is higher than in the experiment. Near the ionization thresholds both calculations give too small a total cross section. Evidently, it is impossible to get perfect agreement with experiment using one free parameter, and we consider the fractional charge $z_e = 0.5$ as a reasonable value

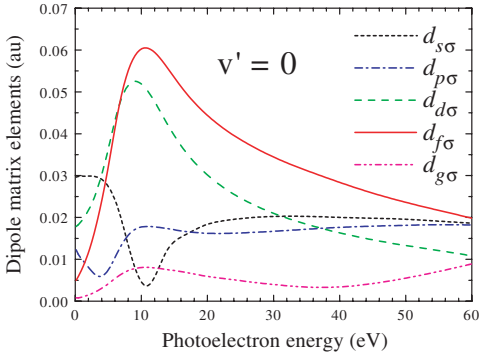

Figure 4. The dipole matrix elements d_i for the first five partial waves of the C K-shell of the CO molecule for transition to the ground vibrational level $v' = 0$ of the final state calculated in the RCHF (0.5) approximation.

giving on average good agreement for different observables. Strong maxima in the region of 300–302 eV photon energy in the experimental cross sections appear due to the two-electron excitations which are not taken into account by the RCHF approximation, therefore they are not reproduced by our theory. Apart from that region, the agreement between theory and experiment is reasonably good both for the total and for the vibrationally resolved cross sections.

The RCHF (0.5) calculation correctly reproduces the absolute magnitudes of the partial cross sections, as well as the shift of the σ^* shape resonance maximum to lower photon energies by about 1.5–2 eV with increasing the vibrational quantum number v' by one. This trend is in accord with the general behaviour of the cross section as a function of the internuclear distance R predicted in [1], namely the maximum of the σ^* shape resonance moves to smaller photon energies with increasing R. In our case the equilibrium internuclear distance for the molecular ion state is smaller than for the ground state [13], and with increasing the vibrational quantum number v' the distances R giving the main contribution to the integral (25) are increasing, as follows from figure 1.

In figure 3 we also present as a thin solid line the total cross section RCHF (0.5) obtained at a fixed equilibrium internuclear distance. Though the influence of vibrational motion is not large, it improves the agreement between the theory and experiment.

3.2. Matrix elements and phase shifts

It is of interest to check which partial wave is giving the main contribution to the σ^* shape resonance. Figure 4 shows the dipole matrix elements $d_{lm} \equiv \langle f_{\varepsilon lm}(\mathbf{r})|d_m|0\rangle$ defined above for σ transitions to the $v' = 0$ final ionic state. In accord with the earlier prediction [3, 21], from our calculation it follows that the main contribution is given by the fσ-wave. On the other hand, the dσ-wave matrix element has also a resonance-like behaviour and nearly the same magnitude, so that the σ^* shape resonance is formed essentially by the contribution of two partial waves, dσ and fσ. Near threshold the sσ-wave gives a predominant contribution. From figure 4 it also follows that in the sσ-wave there is a Cooper minimum similar to that found earlier in the sσ-waves of H_2 [20] and N_2 [11] molecules. The position of this Cooper minimum nearly coincides with the position of the σ^* shape resonance. This behaviour of matrix elements is in general agreement with the conclusions drawn from the analysis of the experimental data presented in [22, 23] where the dipole matrix elements and phase shifts have

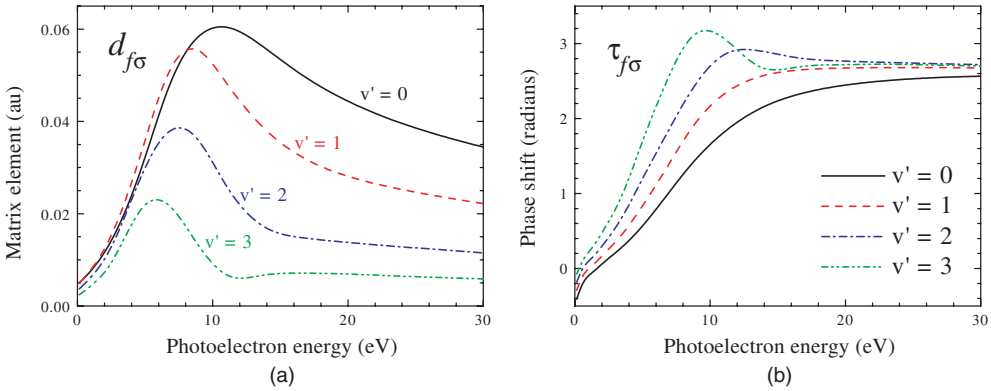

Figure 5. The dipole matrix elements $d_{f\sigma}$ (a) and the short range phase shifts $\tau_{f\sigma}$ (b) for the fσ partial wave for different vibrational transitions.

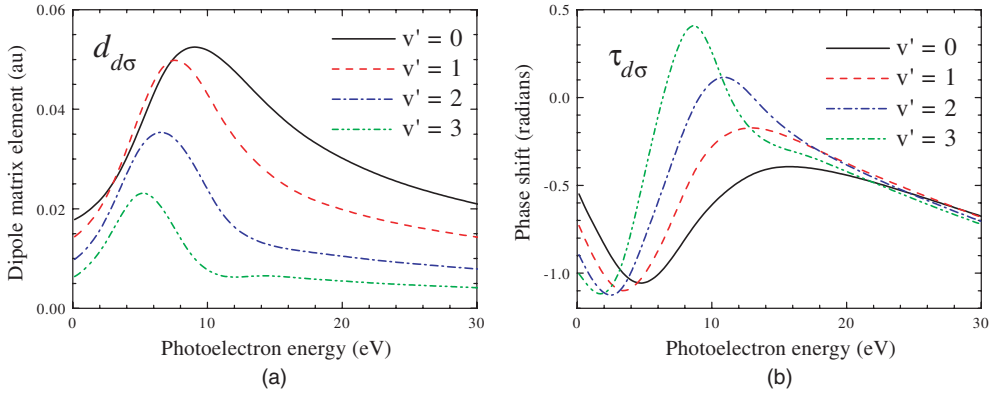

Figure 6. The dipole matrix elements $d_{d\sigma}$ (a) and the short range phase shifts $\tau_{d\sigma}$ (b) for the dσ partial wave for different vibrational transitions.

been extracted from the measured photoelectron angular distributions for fixed-in-space CO molecules. In particular, the existence of the Cooper minimum in the sσ-wave also follows from the analysis in [23]. More detailed comparison of the matrix elements and phase shifts will be presented elsewhere.

Figures 5 and 6 show the dependences of the fσ and dσ dipole matrix elements and the corresponding phase shifts on the vibrational quantum number v'. The short range phase shifts τ are obtained from the equation

$$\tau_{l\sigma} = \delta_{l\sigma} - \eta_l, \tag{27}$$

where $\delta_{l\sigma}$ is the total phase shift, and η_l is the Coulomb part of it, $\eta_l = \arg\Gamma(l+1-\mathrm{i}/k)$. First of all, we would like to stress that while the fσ phase shift is increasing by π as it must be in a resonance [24], this is not the case for the dσ phase shift. It means that only the fσ partial wave shows a truly resonant behaviour in the σ^* shape resonance. Besides that, the behaviour of the dipole matrix elements of the fσ and dσ partial waves with increasing vibrational quantum number v' is very similar. Namely, the positions of maxima of both the fσ and dσ matrix elements are moving to lower energies, and the widths of the peaks are becoming substantially narrower. So, the main peculiarities of the vibrationally resolved cross

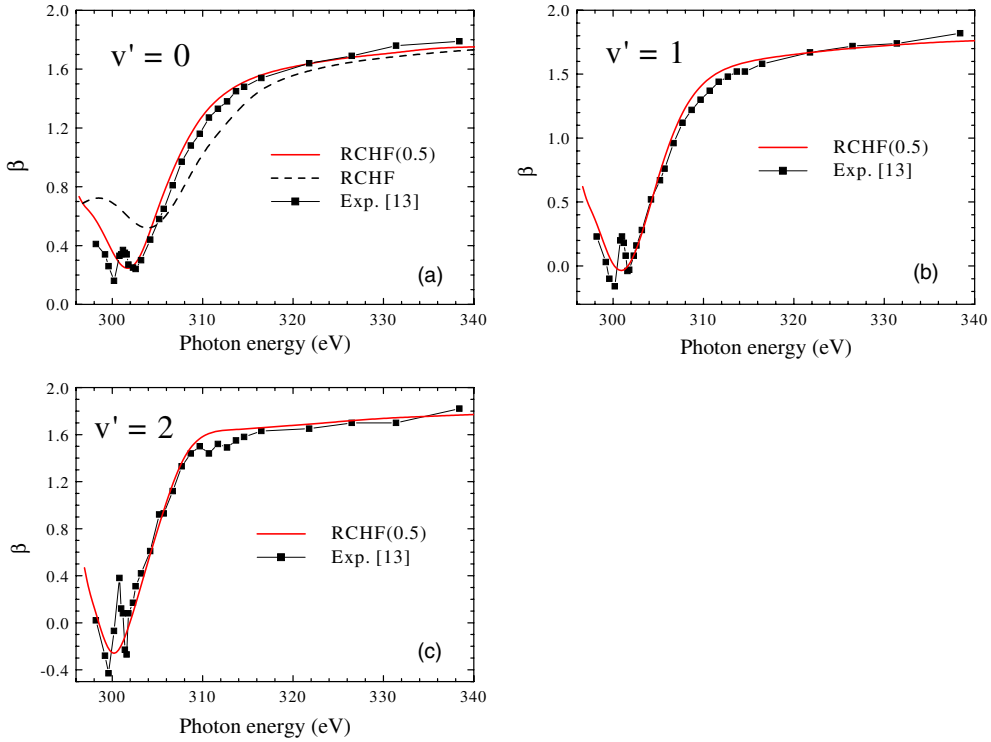

Figure 7. The angular asymmetry parameter β for different vibrational transitions calculated in RCHF (0.5) compared with the experimental data of [13]. In figure 7(a) the RCHF curve obtained with the charge $z_e = 1.0$ is also shown.

sections follow directly from the behaviour of the dipole matrix elements of the fσ and dσ partial waves.

3.3. Vibrationally resolved angular asymmetry parameter

Having the dipole matrix elements and phase shifts, we also calculated the angular asymmetry parameters β given by equation (20) for three vibrational transitions for which there are experimental data [13]. The results are shown in figure 7. The agreement between theory and experiment is even better than for the cross sections, with the exception of the region of the two-electron excitations at about 300–302 eV photon energy which are not taken into account by the RCHF approximation. The theory correctly describes the lowering of the minimum of the β parameter in the region of the doubly excited states and a steady increase (from 1.2 to 1.6 at photon energy 310 eV) with increasing the vibrational quantum number v' from 0 to 2. In figure 7(a) we also show the result of the RCHF calculation with the integer charge 1.0. It is evident that the introduction of the fractional charge improves the agreement with experiment, especially in the region of the shape resonance.

4. Conclusions

The first calculations of the vibrationally resolved partial cross sections and the angular asymmetry parameter β for the C K-shell of the CO molecule have been performed in the

relaxed core Hartree–Fock approximation. It was done by using the fractional charge RCHF method in which the core wavefunctions have been calculated with the charge of the hole equal to 0.5 instead of the usually taken value 1.0. The idea of using the fractional charge originates from the transition state approximation proposed by Slater for molecular calculations some years ago [25]. The value of this charge has been defined from the condition to get the best agreement with experiment in the position of the σ^* shape resonance. The many-electron correlations within the random phase approximation were shown to be negligibly small. The vibrationally resolved partial cross sections are in good agreement with the experimental data published in [13]. In even better agreement are the parameters β for the vibrationally resolved transitions. The calculations show that the predominant contribution to the σ^* shape resonance is given by the fσ and dσ partial waves. The shift of the position of the σ^* shape resonance to lower energies with increasing vibrational quantum number v' is connected with the fact that the equilibrium internuclear distance for the molecular ion state is smaller than for the ground state. Due to that with increasing the vibrational quantum number v' the distances R giving the main contribution to the dipole matrix element are increasing, and that causes the shift of the maximum to lower energies in accord with the conclusion drawn in [1, 2]. In the case of ionization of the O K-shell of CO the situation is the opposite. Namely, the equilibrium internuclear distance for the molecular ion state is larger than for the ground state, so that with increasing vibrational quantum number v' the distances R giving the main contribution to the dipole matrix element are decreasing. That causes the shift of the maximum of the σ^* shape resonance with increasing v' to higher photon energies, as was demonstrated in [15].

Our RCHF calculations are also capable of describing the angular distributions of photoelectrons from fixed-in-space CO molecules corresponding to the vibrationally resolved transitions as was shown recently in [14], though in that case the agreement with experiment is less satisfactory. The fractional charge RCHF method used by us is a rather simple approximation using one free parameter. It would be more straightforward to develop a method for taking into account many-electron correlations beyond the random phase approximation. Though that method will be much more complicated, it must allow us to elucidate the reasons for remaining discrepancies between theory and experiment.

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