Triple Ionization of Carbon Monoxide

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We present theoretical results on the triple ionization of carbon monoxide providing new insights for the understanding of the available experimental data on the triple ionization cross section and the fragmentation patterns of trications. A large number of electronic states are shown to contribute. These are computed by a newly implemented Green's function approach for the efficient *ab initio* calculation of very many triply ionized states needed in the theoretical investigations of molecular multiple ionization processes.

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Multiple ionization of molecules is an interesting example of a transition process within a many-particle system which, because of important correlation effects, often cannot be understood in a simple independent particle picture. The amount of experimental data on multiply charged systems, produced by various techniques like photoionization with synchrotron and intense laser radiation and electron and heavy particle impact, is rapidly increasing [1–4]. One species which is frequently produced in ionization experiments are trications. Because of the strong repulsion of the positive charges these triply positively charged molecular ions are generally unstable. Sophisticated experiments, in which fragments of the dissociation or Coulomb explosion after triple ionization are detected in coincidence, give a detailed picture of these processes. The experimental progress in recent years is not yet sufficiently counterbalanced by theoretical studies, which can be crucial for the interpretation of the experimental findings and also can give clues for further experimental work.

The number of experimentally accessible tricationic states on energy grounds alone is enormous, and there is need to clarify whether or not many of them do contribute to the observations. This large density of states, already for relatively small molecules, is one main difficulty in the theoretical description of triple ionization of molecules. Owing to the possible strong correlation changes and charge localization effects after the loss of three electrons, independent particle methods like Hartree-Fock calculations lack accuracy. Methods which properly account for the correlation effects, but are still based on the computation of individual wave functions and energies, like configuration interaction (CI), rapidly become prohibitively expensive already for moderately large systems. More suitable instruments for the theoretical investigation of transition processes in many-body theories are methods based on Green's functions [5]. They allow the direct calculation of energy differences and transition probability amplitudes within a correlated system. Green's function based methods have proved very useful in studies of singly [6] and doubly [7] ionized cations. In particular, the algebraic diagrammatic construction (ADC) method [8], a general approximation scheme in Green's function theory, has been successfully applied to the one-particle and two-particle propagator which describe the single or simultaneous double ionization, respectively.

The implementation of the second order ADC approximation of the three-particle propagator [9] renders possible the *ab initio* calculation of a very large number of triply ionized states. In this Letter we show that this opens the possibility for the investigation of multiple ionization processes and the understanding of the related experimental observations. After a short description of the theoretical method we present, as a specific example, results on the triple ionization spectrum of the carbon monoxide molecule. Multiple ionization of CO has been studied in various experiments [2–4] (the first few states also theoretically [4]) and triple ionization has been found to play an important role in most of them. The theoretical results presented here, the first of their kind to our knowledge, enable us to gain new insight into these processes which are, as we shall see, governed by the contributions of many electronic states. In particular, we discuss the recently measured electron impact triple ionization cross section of CO [3] and the observed fragmentation patterns of the trication in the light of the new theoretical results.

The three-particle propagator is the quantity which describes the triple ionization in the Green's function approach. In energy space it can be written in the following form [9]:

$$\Pi_{\alpha\beta\nu,\gamma\delta\mu}(\omega) = \langle\Psi_0^N| a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger (\omega - E_0^N + \hat{H})^{-1} \times a_\alpha a_\beta a_\nu |\Psi_0^N\rangle . \tag{1}$$

$|\Psi_0^N\rangle$ is the N-particle ground state with energy E_0^N, $\hat{H}$ is the Hamiltonian of the system, and $a_\alpha^\dagger$ and a_α are creation and annihilation operators. The second order ADC approximation of (1) [9] leads to an eigenvalue problem in the configuration space of the trication, comprising all three-hole (3h) and four-hole–one-particle (4h1p) configurations based on the Hartree-Fock orbitals of the neutral ground state. Details of the implementation of this method are given elsewhere [10]. The vertical triple ionization potentials (TIPs) are given by the eigenvalues; the eigenvectors are related to the Green's function residue amplitudes and permit a full characterization of the tricationic states. A method to extract from these eigenvectors important information about the localization of electron vacancies and the charge distribution in the dense manifold of the cationic states has been developed for the doubly ionized states [11] and extended to the three-hole case [10]. From this three-hole population analysis we obtain the separation of the 3h components of the eigenvectors into contributions describing the localization of the three holes at the same atomic site, at two different atomic sites, and at three different atomic sites (for molecules larger than diatomics). If, for a given state, one of these contributions predominates, the three holes are correspondingly localized, otherwise the charges are delocalized over a part of or the whole molecule.

We have calculated a large number of TIPs using the equilibrium bond distance of the CO ground state $R_0 = 1.128$ Å [12] and a triple-zeta valence $[5s, 3p]$ contracted Gaussian basis set augmented with one d function on each atom (TZVP basis) [13]. The matrices are sufficiently small to be fully diagonalized with standard routines. For larger systems this is no longer possible and carefully optimized diagonalization routines based on block Lanczos or block Davidson algorithms [14] are used to compute a large number of eigenvectors and eigenvalues. This calculation yields some thousands of TIPs and the corresponding eigenvectors. We wish to stress that comparable CI calculations for, say, only some dozens of TIPs would be an extremely cumbersome task.

A first relevant example of the questions that our calculations may cast new light upon is offered by the recent coincidence measurement of the dissociation products of CO^{3+} obtained by electron impact, yielding the triple ionization cross section [3]. The cross section is proportional to the square of the transition matrix element for the transition from the initial to the final state, to the density of final states, and to the reciprocal of the incident velocity [15]. An exact calculation of the relevant quantities is at present beyond the capacity of theory even for only one accessible triply ionized state. On the other hand, we can make use of the fact that the density of tricationic states is high and at a given energy soon above the triple ionization threshold a large number of states should contribute to the triple ionization cross section. The total triple ionization cross section should therefore be the sum of a large number of contributions and the shape of a single contribution may be of minor importance. The simplest model is that each tricationic state contributes to the cross section with the same, energy independent value above the corresponding triple ionization threshold. This is, of course, a very crude approximation and certainly not correct for any individual state but may be reasonable as an average over a large number of states. In this simple picture the total triple ionization cross section is given by $\sigma(E) \propto N(E)/\sqrt{E}$, where $N(E)$ is the integrated density of states and E is the impact energy ($\sqrt{E}$ is the incident velocity).

Figure 1 shows the triple ionization cross section calculated as described above, with TIPs obtained from an ADC calculation in the TZVP basis, together with the experimental results of Spekowius and Brehm [3]. Since we do not distinguish between the two different dissociation channels ($C^{2+}O^{+}$ or $C^{+}O^{2+}$) the two experimental cross sections for the different fragmentation products are summed. Neither the experimental nor the theoretical cross section are on an absolute scale and are adjusted to the same maximal height. The ionization of core electrons is not considered. Multiple ionization involving the core has low probability due to core-valence separation, and in addition core vacancies decay very fast and will not be observed.

The theoretical results based only on the distribution of the computed TIPs reproduce well the main features of the experimental data; especially the position of the maximum of the cross section is in surprisingly good agreement. At high impact energies the cross section is overestimated by our calculations which may be attributed to the fact that the triple ionization probabilities for the individual states should decrease with sufficiently high impact energy, whereas we used constant probabilities. Above a TIP of 375 eV no tricationic states are computed (if core ionization is not considered) so that from this energy onward the theoretical cross section falls off with $1/\sqrt{E}$. At low impact energy the experimental cross section increases somewhat steeper than calculated. This may be explained by different triple ionization probabilities for differently

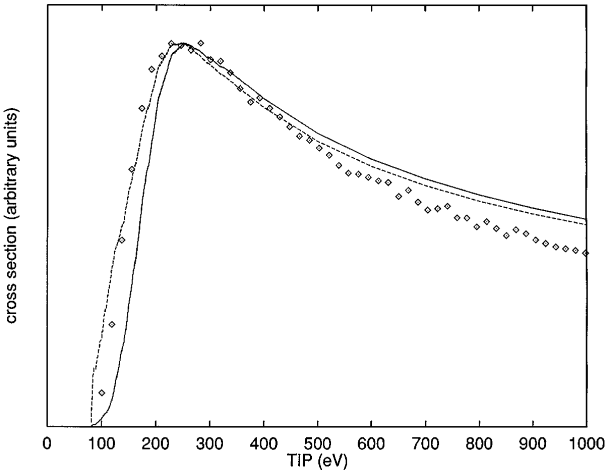

FIG. 1. Electron impact total triple ionization cross section of carbon monoxide. The solid line is the theoretical result obtained by giving each state the same, energy independent, triple ionization probability. For the dashed line a 50 times higher triple ionization probability is assumed for the 3h configurations with respect to the 4h1p configurations. The diamonds are the experimental results [3] obtained by summing the data for the two dissociation channels.

excited final states, as we now discuss in some more detail. As mentioned above, the configuration space of the calculations comprises all 3h and 4h1p configurations based on the neutral Hartree-Fock ground state. There is, of course, an infinite number of higher excited tricationic states (e.g., Rydberg series), which is not taken into account. However, processes in which, beside the simultaneous ejection of three electrons, one or more electrons are highly excited should have a much lower probability than those corresponding to 3h final states. Therefore the states which are not calculated should be of minor importance for the triple ionization cross section. By the same argument, the contributions of the tricationic states which are dominated by 4h1p configurations are possibly overestimated by counting them with the same probability as the states dominated by 3h configurations. This can be approximately corrected for by giving each state a triple ionization probability proportional to the total three-hole pole strength, i.e., the sum of the square coefficients of the 3h configurations of the corresponding ADC eigenvector. Since the tricationic states with a large total three-hole pole strength are concentrated on the lower energy part of the triple ionization spectrum, this affects mainly the first part of the calculated cross section. In Fig. 1 we have included the result of a calculation under the assumption that the 3h configurations have a 50 times larger triple ionization probability than the 4h1p configurations. As can be seen this does not change the shape of the curve much but visibly improves the agreement in the steeply increasing low energy region.

Our results strongly suggest that the shape of the cross section is essentially dictated by the form of the dense energy distribution of triply ionized states, independent of the actual number of contributing states. A straightforward and meaningful test of this indication suggests itself, namely, the analysis of the basis set dependence of the computed results. We have therefore repeated the computations using two other basis sets, obtaining cross section curves essentially indistinguishable from the ones in Fig. 1 [10].

Above the quadruple ionization threshold (which we have computed by CI to be about 140 eV; the atomic values are 148 eV for carbon and 181 eV for oxygen [16]) the tricationic states can, in principle, decay under emission of another electron. If this happens before the detection of the fragments, this process does not contribute to the measured cross section. We found the contributions of higher lying tricationic states to be important for the reproduction of the experimental cross section, indicating that the lifetimes of these states are sufficiently long. Unfortunately no values of the lifetimes in question are available to confirm this result.

The present results also give very useful guidelines for the interpretation of another peculiar experimental observation, concerning the dissociation channels of CO^{3+}. The different fragmentation channels after triple ionization can be observed separately in coincidence experiments [2,3]. It has been found that fragmentation leading to $C^{2+} + O^{+}$ occurs much more frequently than a fragmentation to $C^{+} + O^{2+}$. The three-hole population analysis that we have performed clearly shows that this fact must be fully attributed to the dissociation dynamics. In Fig. 2 the result of the population analysis of the lowest states with a total three-hole pole strength greater than 0.1 is shown. The different contributions are designated by the number of holes on each atom; for example, $C^{-2}O^{-1}$ means two holes localized at the carbon and one at the oxygen atom. As can be seen from Fig. 2, after the vertical transition to the triply ionized CO molecule all states but one are characterized by a delocalization of the charges (this is true for all states, not only for those shown in Fig. 2) with, in fact, a slight predominance of the $C^{-1}O^{-2}$ character. Clearly, the character of the charge distribution after vertical triple ionization does not explain the large predominance of one fragmentation channel, as is also supported by the fact that the same predominance has been observed with different projectiles and over a wide range of impact energies.

To obtain more information about the dissociation process we have carried out valence complete active space self-consistent field (CASSCF) calculations followed by single and double excitations CI [17] on the potential energy curves of the lowest tricationic states of CO^{3+} [10]. No previous work is, to our knowledge, available on this subject. Some results for the states of $^2\Pi$ symmetry are shown in Fig. 3. Already the lowest states are subject to strong interactions exhibiting a number of avoided curve crossings, which can be seen clearly in Fig. 3. Because of this interaction the character of the states changes drastically during the dissociation process. Indeed the states shown in Fig. 3 dissociate to $C^{2+} + O^{+}$ independent of their character after the vertical transition. At the vertical transition some of the states shown are dominated by O^{-3} and $C^{-1}O^{-2}$ contributions of the population analysis (see Fig. 2) and consequently have a charge distribution after the vertical process which is very different from that of the asymptotic states. Similar results hold for other state symmetries, due to the fact that the lowest $O^{2+} + C^{+}$ asymptote lies about 11 eV above

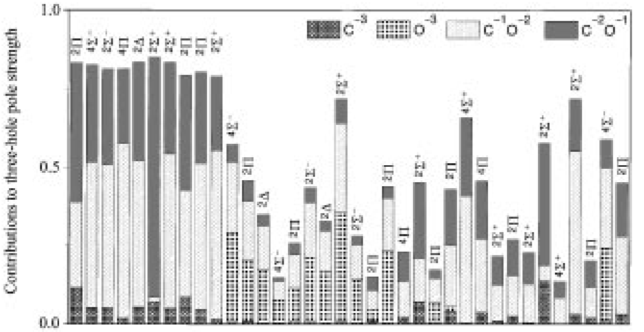

FIG. 2. Three-hole population analysis for the lowest tricationic states with a total three-hole pole strength greater than 0.1. The different contributions are designated by the number of holes on each atom; for example, $C^{-2}O^{-1}$ means two holes localized at the carbon and one at the oxygen atom.

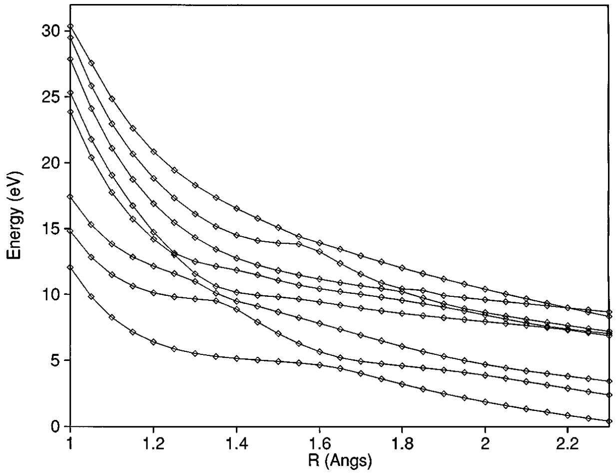

FIG. 3. Computed potential energy curves for the lowest tricationic states of symmetry $^2\Pi$ of CO. The energy of the lowest point is taken as the zero of the energy scale.

the lowest $C^{2+} + O^{+}$ dissociation channel [16]. Some of the potential energy curves are quite flat and may even have a shallow minimum. Figure 3 suggests that some diabatic curves have minima (probably those leading to the high asymptotes with three holes on one atom) which disappear upon interaction with the repulsive states. The presently accessible experimental data give no evidence for a metastable CO^{3+} ion.

In this paper we have given strong evidence that a vast number of molecular tricationic states are produced in experiments with high energy projectiles. It is, therefore, insufficient to interpret available experiments by discussing the first few tricationic states as is usually done. Hundreds or even thousands of states are of relevance. Our second concluding remark concerns the dissociation dynamics. Much work is reported on measured distributions of kinetic energy release in the dissociation of highly ionized molecules and discussed in terms of Coulombic and non-Coulombic potential curve models [1,2,4]. The present calculations show that up to a very high energy the potential curves have complex structures and exhibit multiple avoided crossings. It becomes evident that the nuclear dynamics "following" ionization does not proceed on these potential curves, in general. In particular, if the driving force at the vertical geometry is large, i.e., the curve in question is steep, the nuclei acquire sufficient momentum to frequently jump from one curve to another owing to the nonadiabatic coupling among the corresponding states. Because of the large number of curves involved, a broad distribution of kinetic energy release peaked approximately at Coulombic values results. Again, simple models based on a few individual curves insufficiently explain the underlying rich dynamics, and more detailed experiments and theory are needed.

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