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Towards a spectroscopy of doubly charged ions

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In the light of a recent demonstration that a two-electron symmetry rule governs final-state selection in the double photoionization of argon, we re-examine current interpretations of molecular doubly charged ion spectra. New double-ionization data from photoionization and charge-exchange experiments on O_2 and C_2H_2 augment the number of centrosymmetric molecules on which the application of the selection rule can be tested. Results do not contradict a rule that photoionization of closed-shell molecules populates chiefly triplet gerade or singlet ungerade states of doubly charged ions.

1. INTRODUCTION

Molecules that lose two electrons as a result of an energetic encounter remain as doubly charged ions only under special circumstances. Because all are highly reactive as powerful oxidizing agents they can be kept only either in a vacuum or in a superacid medium. Even in such favourable environments, many doubly charged ions have very short lifetimes, and very few support bound electronically excited states. Because of these characteristics, spectroscopic techniques that rely on the existence of long-lived species can be applied to only a limited subclass of doubly charged ions. Optical emission is known for only three species, N_2^{2+} (Carroll 1958), NO^{2+} (Besnard *et al.* 1986) and O_2^{2+} (Tohji *et al.* 1986). To explore the term schemes of the majority of doubly charged molecular ions it is therefore necessary to measure the energies needed to form them from other well-defined species. They are formed directly from ground-state neutral molecules by photoionization and double-charge transfer, from an ionic core-hole state in Auger spectroscopy and from a normal singly charged ion in charge-stripping spectroscopy. Each of these techniques has its special characteristics. Double-charge transfer to H^+ strictly conserves spin and so populates singlet states exclusively for closed-shell light-atom species (Appell *et al.* 1973; Moore 1973, 1974), but seems, according to recent results, to populate almost all available singlet states (Millié *et al.* 1986). Within the multiplets arising from single electron configurations, Auger transitions also populate singlet states preferentially, although triplets are not entirely excluded (Thomas & Weightman 1981), whereas charge stripping (Porter *et al.* 1981) presumably populates both singlets and triplets equally. The characteristics of double ionization by single photons, which are the subject of this paper, are still not understood. It has become clear that photoionization populates at least ground triplet states of several doubly charged ions (CS_2^{2+}, CO_2^{2+}, H_2O^{2+}, CH_4^{2+}) and the singlet ground state of one (NH_3^{2+}) (Eland *et al.* 1986), but no paradigm has hitherto emerged.

In this paper we set out to examine the systematics of photo-double ionization of molecules with the help of new experimental data, and in the light of a recent demonstration that a strong selection rule operates in the double photoionization of atoms (Lablanquie *et al.* 1987).

2. Experimental principles

Double ionization can be studied in the inevitable presence of single ionization either by observation of a stable doubly charged product, by recognition of the removal of two electrons, or by detection of two singly charged ions in coincidence. In double-charge-transfer spectroscopy (Appell *et al.* 1973), two-electron exchange is selected by using H^+ projectiles and detecting H^- specifically, from the process

$$H^+ + M \rightarrow H^- + M^{2+}.$$

The energy required to effect the charge transfer is abstracted from the translational energy of the proton, and is determined from the kinetic energy of the H^- ion measured at a very small scattering angle. Overall two-electron transfer can also occur in two sequential stages, each of which produces singly charged ion, but such interfering processes are easily recognized and eliminated by their quadratic pressure dependence. Their energy requirements can be accurately predicted from the photoelectron spectrum of M, and provide a useful energy calibration.

Double ionization by photon impact can sometimes be recognized by observation of a doubly charged ion in the mass spectrometer; normally it is necessary to detect, in coincidence, two particles of the same sign from the reaction

$$M + h\nu \rightarrow M_1^+ + M_2^+ + 2e^-.$$

In photoion–photoion coincidence (PIPICO) spectroscopy (Dujardin *et al.* 1984; Curtis & Eland 1985), ionization is brought about in a strong uniform electric field, which accelerates ions into the drift tube of a time-of flight mass spectrometer. The arrivals of correlated ion pairs are recorded as a function of the time difference between them, which is centred on a time difference proportional to the difference in square roots of the ion masses. The arrival-time difference has a dispersion caused by the kinetic energy released in formation of the ion pair, as in normal time-of-flight mass spectrometry (Franklin *et al.* 1967), from which the magnitude of the energy release can be deduced. Multiple energy releases can sometimes be recognized from the shape of the peaks; this can be done reliably, and energy-release distributions can be determined, by restricting detection to those pairs that dissociate along the mass-spectrometer axis (Richardson *et al.* 1986), although this technique is very costly in experimental run time. Once the kinetic-energy release is known it can be added to the energy of the (assumed) dissociation products to provide an estimate of the energy of the precursor doubly charged ion. The yield of the correlated pairs can also be measured as a function of wavelength and the threshold energy for each dissociative double ionization reaction can be determined.

A more direct determination of the doubly charged ion energy can be made by a photoelectron–photoelectron coincidence (PEPECO) experiment, in which two energy-analysed electrons are detected in coincidence. The energy balance is completely defined by

$$h\nu = A(\mathrm{m}^{2+}) + E_1 + E_2,$$

and is exactly analogous to the energy balance in photoelectron spectroscopy. Because of the low overall collection efficiency for energy-resolved electrons this is a very difficult experiment, however, and special strategies are needed to make it practicable. A new apparatus at Oxford uses two large hemispherical analysers, which will analyse electrons after acceleration in special lenses designed to accept electrons from a very large solid angle. An alternative strategy, which has enabled the first successful PEPECO experiments at Orsay (Lablanquie *et al.* 1987) is to selectively detect one electron of near-zero kinetic energy, and energy analyse the other. If ionization takes place in a weak electric field, all zero-energy electrons are accelerated parallel to the field lines, and can be detected with very high efficiency in a restricted solid angle. Faster electrons that happen to be ejected into the acceptance angle can be rejected after detection, because their flight times, measured from the time of a light pulse, deviate from the expected value (Morin *et al.* 1980). The efficiency of this 'threshold' electron detection is so high that even with a relatively inefficient 127° cylindrical condenser analyser for the second electron, the electron–electron coincidence experiment proved possible. The interpretation of results from experiments with this configuration does rely on the theoretical prediction (Read 1985), which was, however, directly confirmed, that the electrons ejected in direct double ionization near threshold have a flat distribution.

Experimental details of the double-charge-transfer method (Fournier *et al.* 1985) and of the photoionization techniques (Lablanquie *et al.* 1985) have been given elsewhere, and are not repeated here.

3. RESULTS

This section begins with a review of relevant previous results from PIPICO, double-charge-transfer experiments and the first PEPECO experiment, after which new data on O_2 and C_2H_2 double ionization are presented.

3.1. *Existing data*

The PIPICO technique has been in use for over three years, and detailed studies of ten molecules have been published, with less extensive results on some dozen others (for a review, see Eland *et al.* 1986). In every case of dissociative double ionization where the precursor doubly charged ion energy could be estimated both by addition of a measured kinetic-energy release to the lowest dissociation asymptote and by direct determination of the reaction threshold, the two estimates are in sufficiently close agreement to confirm that ground-state products are formed. It is noticeable that this is true even in cases where the Wigner–Witmer correlation rules predict otherwise (H_2O^{2+}, Richardson *et al.* 1986; CH_4^{2+}, Fournier *et al.* 1985). Some internal excitation of the products is certainly involved, and the uncertainties and spread of kinetic-energy releases still leave the possibility of electronic excitation open in some cases (CO_2, Dujardin & Winkoun 1985; NO_2, Eland *et al.* 1986). Nevertheless, the usefulness of the kinetic-energy measurement as an estimator of doubly charged ion-state energies is confirmed. In addition to the magnitude of the energy release, the width of the Franck–Condon zone can be estimated from the spread of kinetic energies, and the partial cross section for formation of each state is given by the abundance of products with a particular energy. Thus although the PIPICO technique is indirect, it leads to a view of the spectrum of a doubly charged ion containing, in principle, all the information that would be given by a direct photoionization method. As an example, a simulated vertical photoionization spectrum of CS_2 is shown in figure 1, where it is compared with a double-charge-transfer spectrum.

Double-charge transfer to fast H^+ ions seems to populate all, or at least most, singlet states of a doubly charged ion. The relative intensities are distorted by a strong fall-off of the cross

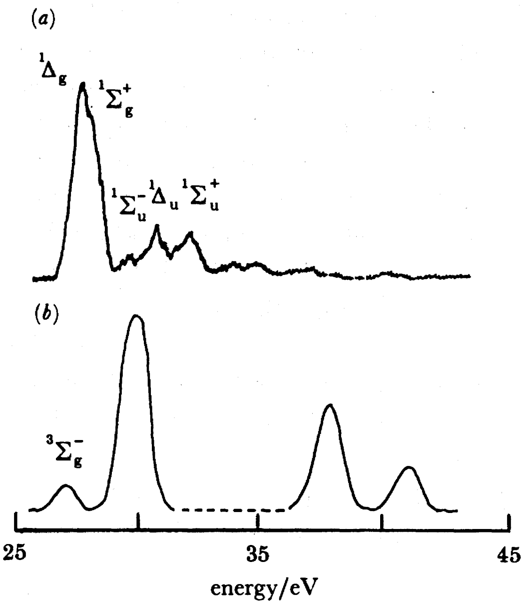

FIGURE 1. Double-charge-transfer (DCT) spectrum (*a*) of CS_2 at an H^+ energy of 2 keV, and a simulated double photoionization (PI) spectrum (*b*) for a photon energy of 50 eV.

section at higher energies, for which no compensation can be made. The fall-off is less rapid at higher projectile energies, but at the cost of diminished resolution.

Figure 1 exemplifies the fact that rather few states are populated by double photoionization. They are not the same states as seen in double-charge transer, nor certainly all the accessible states as calculated by *ab initio* theory. The state identifications already marked on figure 1 have been arrived at by comparison with extensive SCF-CI (self-consistent field–configuration interaction) calculations (Millié *et al.* 1986). According to the calculations the second, and most intensely populated, state in photoionization must be one or more out of $^1\Sigma_u^-$, $^3\Sigma_u^-$, $^3\Delta_u$ or $^3\Sigma_u^+$ arising from the dominant configuration $\pi_u^3\pi_g^3$. Until now we have had no means of deciding which of these states is involved.

A hope of understanding the selectivity of double photoionization is offered by the results of the PEPECO experiment on argon by Lablanquie *et al.* (1987). They discovered that of the three states ^3P_g, ^1D_g and ^1S_g of Ar^{2+} arising from the p^4 configuration only ^3P_g is significantly populated by photoionization at a photon energy of 56 eV. This observation, which was not expected by the experimenters, actually confirms the theoretical predictions of several groups (Greene & Rau 1982, 1983; Stauffer 1982; Read 1985) in connection with Wannier theory that only certain symmetries of the two-electron wavefunction are favourable to two-electron escape from a positively charged atom. The optimum configuration, called the Wannier point, requires the electrons to remain equidistant from that ion with equal radial velocities at 180° to each other. Unless the three quantum numbers L, (total orbital angular momentum), S (total spin) and Π (parity) are all even or all odd, the two-electron wavefunction has a node at the Wannier point and double ionization is disfavoured. When the dipole selection rule is applied to double photoionization of argon, it is found that only the ^3P_g state of Ar^{2+} can be formed together with one of the favourable electron wavefunction symmetries ^1S_g, ^3P_u, ^1D_g and so on. We now attempt to generalize this rule to molecules.

For photoionization of a closed-shell molecule possessing a centre of inversion, the atomic-symmetry requirement implies a simple rule that states of the double-charged ion formed will be of even (g) parity if spin triplets, or of odd (u) parity if singlets. The reduction in symmetry seems to remove all force from the orbital angular-momentum restriction. The rule can be applied to the CS_2^{2+} spectrum in figure 1, and eliminates $^3\Sigma_u^-$, $^3\Delta_u$ and $^3\Sigma_u^+$ as likely identifications for the second peak, leaving only $^1\Sigma_u^-$. The formation of the ground state of CS_2^{2+}, $^3\Sigma_g^-$, which is observed, is also allowed according to the rule.

If the state near 30 eV populated by photoionization is indeed $^1\Sigma_u^-$, we have three independent estimates of its energy. From the $CS^+ + S^+$ threshold 30.2 ± 0.4 eV, from the kinetic-energy release in PIPICO 30.7 ± 1 eV and from the double-charge transfer spectrum 30 ± 0.3 eV, which are in very good agreement.

Similar reasoning applied to present evidence on CO_2 double photoionization leads to a similar conclusion. It is certain that the ground state of CO_2^{2+}, $^3\Sigma_g^-$, is populated by photoionization, and the next strong population appears at 39.7 ± 0.5 eV as the threshold for $CO^+ + O^+$ formation, close to a feature at 40.6 ± 0.3 eV seen in double-charge transfer. From the estimated accuracy of the energy normalized SCF-CI calculations (Millié *et al.* 1986) the state involved must be either $^1\Sigma_u^-$ from the $\pi_u^3\pi_g^3$ configuration or $^1\Sigma_g^+$ from $\pi_u^4\pi_g^2$. Application of the selection rule evidently favours the identification as $^1\Sigma_u^-$, contrary to previous conclusions.

Few other centrosymmetric molecules have yet been examined by double-photoionization techniques in sufficient detail for any test to be made. We have therefore re-examined the PIPICO spectra of oxygen and ethyne (acetylene).

3.2. *Oxygen*

An early PIPICO study of oxygen (Curtis & Eland 1985) showed several distinct energy releases in $O^+ + O^+$ formation after He II ionization. Because of the large number of available states of O_2^{2+} calculated by Beebe *et al.* (1976) and uncertainty as to whether their dissociations are homogeneous, no definite interpretation could be arrived at. Several energy releases were also found after electron impact ionization of O_2 by Brehm & de Frênes (1978) and by Curtis & Boyd (1984) who also studied collision-induced dissociation of O_2^{2+}. There is only partial agreement between the different sets of energy releases, and the PIPICO data seem to be unique in showing energy releases less than 6 eV.

To clarify this we have remeasured the PIPICO spectrum of O_2 both under He II conditions with good resolution for kinetic energies, and also at three selected wavelengths. The results are presented in figure 2. At the longest wavelength, 326 Å† (38 eV) there is a single energy release of 4.5 ± 0.2 eV, which can only arise from ground-state O_2^{2+} ($^1\Sigma_g^+$) dissociating to ground-state products, $2O^+$ (^4S). Because some O_2^{2+} ions formed by photon impact and electron impact are known from mass spectrometry to have lifetimes at least as long as a few microseconds, it seems that the rapid dissociation responsible for the PIPICO signal must come from excitation to part of the O_2^{2+} ($^1\Sigma_g^+$) state outside the potential well. At 304 Å (40.8 eV) we find two energy releases; the 4.5 eV release is still present, but a release of 7.2 ± 0.5 eV gives more abundant $O^+ + O^+$ pairs. According to the calculation of Beebe *et al.* (1976), the state that is most likely to be formed by a vertical transition at this photon energy is $^3\Sigma_u^+$, which is also the only other state (among singlets and triplets) that correlates to ground-state products. The observation positively confirms that this state is formed, because any state correlating with excited products but releasing 7.2 eV would have to lie above $7.2 + 35.7 = 42.9$ eV, and thus above the actual

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† 1 Å = 10^{-10} m = 10^{-1} nm.

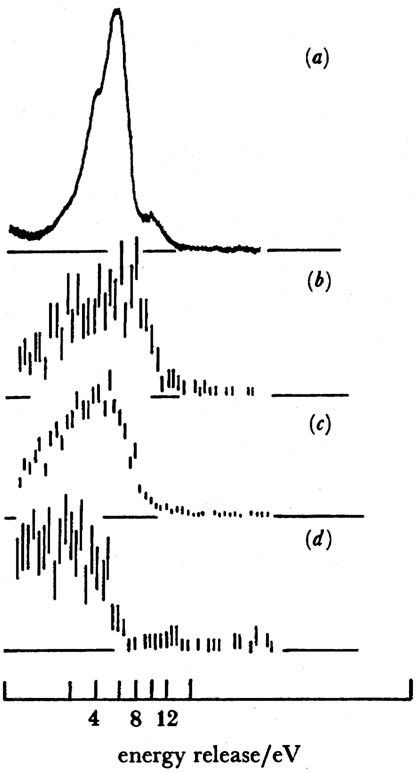

FIGURE 2. PIPICO spectra for dissociative double ionization of O_2 ($O_2^{2+} \rightarrow O^+ + O^+$) at the wavelengths (*b*), 25.6 nm; (*c*) 30.4 nm; and (*d*) 32.6 nm. The uppermost spectrum, (*a*), taken with filtered HeII light, is a differential spectrum, whereas the other spectra are of integral form.

photon energy. These PIPICO observations quite definitely locate Franck–Condon zones of the first two states of O_2^{2+}. At the higher photon energy of 48 eV (256 Å) the energy-release distribution closely resembles the one observed with filtered HeII light, including at least three energy releases including 4.5 eV, 7.2 eV and one or more energies near 9.5 eV. The theoretical calculations indicate that more than twelve states of O_2^{2+} are accessible at this energy, but only a few correlate to such low-energy ion-pair products as to release more than 7 eV of kinetic energy.

From the PIPICO results we deduce that part of the Franck–Condon region of the $^1\Sigma_g^+$ ground state of O_2^{2+} is at 36.8 ± 0.2 eV, which is in satisfactory agreement with the electron-impact appearance potentials of O_2^{2+} reviewed by Curtis & Boyd (1984). We locate the $a^3\Sigma_u^+$ state at 39.5 ± 0.5 eV; this may be the state that produces the first Auger peak, at 38.3 eV (Moddeman *et al.* 1971) and may be the terminus of optical emission (Tohji *et al.* 1986). The double-charge-transfer spectrum, remeasured recently at high resolution, contains resolved peaks at 41.1 and 43.3 eV, but not at 36.8 or 39.5 eV. Because the excitation of both $X^1\Sigma_g^+$ and $a^3\Sigma_u^-$ is forbidden in double-charge transfer (Appell *et al.* 1973), this is in agreement with the present assignment. The states at 41.1 and 43.3 eV are probably higher triplet states, whose formation by photon impact may also be possible at short wavelengths.

Because the ground state of O_2 is $^3\Sigma_g^-$, the simple symmetry rule for double photoionization does not apply. Instead we require the two-electron wavefunction symmetry to be one of ^1S_g, ^3P_u or ^1D_g, and then consider which O_2^{2+} states when combined with these symmetries give rise to the dipole-allowed ${}^3\Sigma_u^-$ or ${}^3\Pi_u$ overall states. The conclusion is that both ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$, whose formation is proven, are indeed allowed. Many of the higher-energy states are also allowed, and only ${}^1\Sigma_u^-$, ${}^1\Delta_u$ and ${}^1\Pi_u$ are forbidden, so the identity of the states producing the highest-energy O^+ ions cannot yet be ascertained.

3.3. *Ethyne*

The PIPICO spectra of ethyne and ethyne-d$_2$ have been examined by using filtered He II radiation (Eland *et al.* 1986), but have not previously been analysed for the energies of the $C_2H_2^{2+}$ states. The intense two-body reactions forming $C_2H^+ + H^+$ and $CH^+ + CH^+$ from C_2H_2 both release kinetic energies which point to a precursor state at 36 ± 0.5 eV (figure 3). The weak three-body dissociations indicate another state at about 41 ± 1 eV. The ground state of $C_2H_2^{2+}$ is ${}^3\Sigma_g^-$ (Pople *et al.* 1982) and is known to lie near 32.7 eV (Appling *et al.* 1985); at least some, possibly all, ions in this state are stable and therefore do not appear in the PIPICO spectrum. We do, however, clearly observe C_2HD^{2+} ions in the mass spectrum of monodeuteroacetylene under He II photoionization, and consider formation of ground-state doubly charged ions to be the most likely explanation of its presence.

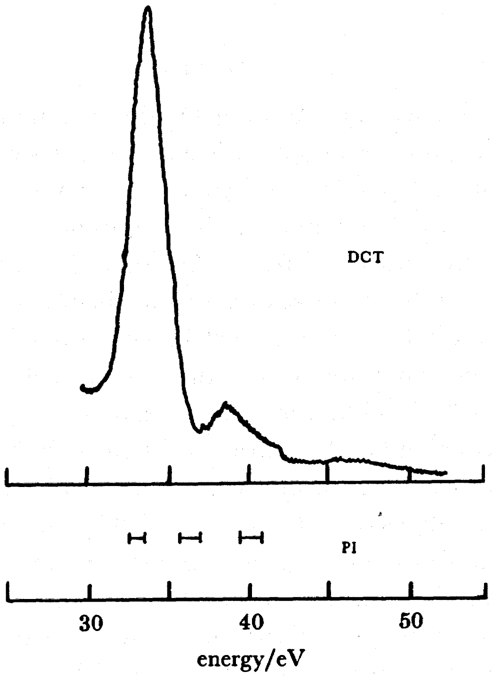

FIGURE 3. DCT spectrum of acetylene, $C_2H_2^{2+}$, and the energies at which photoionization is deduced to occur. High intensity at the low-energy side of the DCT spectrum is caused by interfering two-fold single-ionization processes.

The states of $C_2H_2^{2+}$ accessible by two-electron abstraction from the outermost orbitals of ethyne include only four whose formation would be expected to be favoured according to the symmetry-based rule for photoionization. These are ${}^3\Sigma_g^-$ (ground state) from $\sigma_u^2\sigma_g^2\pi_u^2$, ${}^1\Pi_u$ from $\sigma_u^2\sigma_g\pi_u^3$, ${}^3\Pi_g$ from $\sigma_u\sigma_g^2\pi_u^3$ and ${}^1\Sigma_u^+$ from $\sigma_u\sigma_g\pi_u^4$.

To clarify which states are responsible for the dissociative double ionization of ethyne we have re-examined the double-charge-transfer spectrum at higher resolution than before (Appell *et al.* 1974) and have also instituted new SCF calculations. The double-charge-transfer spectrum (figure 3) shows $C_2H_2^{2+}$ states, which according to the usual selection rule must be singlets, at 33.7, 38.4, 41 and 45.9 eV. The state at 41 eV is seen only as a weak shoulder in the spectrum; it is within range of the energy of 41 ± 1 eV deduced from the PIPICO results, suggesting that this state may be $^1\Pi_u$, or $^1\Sigma_u^+$. The other states seen in photoionization and double-charge transfer do not coincide, and the supposition must be that the 36 eV state, strongly populated in photoionization, but not by charge transfer is a triplet, perhaps $^3\Pi_g$.

To test the plausibility of this assignment we have carried out SCF calculations on $C_2H_2^{2+}$ in a 6-31G** basis. The vertical excitation energies to the first seven states of $C_2H_2^{2+}$ from neutral C_2H_2 are calculated to be 29.3 eV ($^3\Sigma_g^-$), 30.5 eV, ($^1\Delta g$), 31.7 eV ($^1\Sigma_g^+$). 36.5 eV ($^3\Pi_u$), 37.4 eV ($^1\Pi_u$), 38.6 eV ($^3\Pi_g$) and 39.8 eV ($^1\Pi_g$). As these are pure SCF calculations without any CI it is not surprising that the lowest state is calculated 3.4 eV lower than the measured appearance potential, and we attempt a first confrontation with experiment by scaling all the energies by +3.4 eV. The scaled calculated energy of the $^1\Pi_u$ state is then 40.9 eV, in very good accord with the DCT feature and the PIPICO result of 41 ± 1 eV. The other bands do not match, however, and both $^3\Pi_u$ and $^3\Pi_g$ appear too high to match the PIPICO energy of 36 eV; we are attempting more sophisticated calculations before making a more detailed comparison.

4. Discussion

It is inherently likely that the two-electron wavefunction symmetry, now confirmed to control the direct double photoionization of argon, will also have a strong influence on the direct double ionization of molecules. The effect of such a symmetry restriction can only be to limit the number of dication states strongly populated, in accordance with experimental results. The evidence, which comes from the paucity of distinct kinetic-energy releases in dissociative double ionization, and to a lesser extent from simple straight-line behaviour in double-photoionization cross sections is, however, indirect and could yet be confounded. Many distinct ionic states could release the same kinetic energy by dissociating on parallel surfaces to excited products, and structure in cross-section curves is notoriously unreliable as a guide to ion states. The data on CO_2, CS_2, O_2 and C_2H_2 examined here are consistent with the application of the atomic symmetry rule to these centrosymmetric molecules, but problems still remain. In CO_2^{2+}, for instance, theory predicts two 'allowed' states of $^3\Pi_g$ and $^1\Pi_u$ symmetry near 43 eV, but no sign of them is seen in the photoionization data. Furthermore, the small number of doubly charged ion states in photoionization seems to be a property of centrosymmetric and non-centrosymmetric molecules equally, whereas if the parity rule is dropped the selection rule loses almost all its force. Double photoionization of OCS, SO_2, NH_3, H_2O and CH_4, which are the only molecules yet examined in detail, results, on present evidence, in no more catholic choice of final states than photoionization of centrosymmetric congeners.

Besides the experimental uncertainty, which we have good hope of resolving with the new generation of PEPECO experiments, there is a fundamental question of theory. The electron-pair symmetry rule applies only to direct double photoionization near threshold, and not to Auger-like processes. There is good reason to expect that the selection rules in Auger processes will be different, and it is not yet known whether such processes become important only after inner-shell thresholds, or earlier. As molecular complexity increases, the scope for indirect double ionization involving deep-lying molecular orbitals of the valence shell and inner valence shell must also increase, and it would not be surprising if for large molecules indirect double ionization dominates the direct process even in the range of valence states of the doubly charged ions. At high energies, where inner-shell holes can be created, it is certain that indirect double ionization will be dominant. The role of theory in the advance of this field will be crucial: we now have the means to calculate the energies of molecular and ionic states with really useful accuracy, but the calculation of transition probabilities for double ionization seems to lag behind.

5. Conclusions

Analysis of the present PIPICO and other data is not inconsistent with the idea that the selection rule developed for two-electron escape from atomic ions also applies to molecular double photoionization of small centrosymmetric molecules. If it is confirmed and perhaps extended, the rule will be of great importance in the interpretation of doubly charged ion spectra.

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