# Synchrotron radiation VUV double photoionization of some small molecules*

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The VUV double photoionizations of small molecules (NO, CO, $CO_2$, $CS_2$, OSC and $NH_3$) were investigated with photoionization mass spectroscopy using synchrotron radiation. The double ionization energies of molecules were determined with photoionization efficiency spectroscopy. The total energies of these molecules and their parent dications ($NO^{2+}$, $CO^{2+}$, $CO_2^{2+}$, $CS_2^{2+}$, $OSC^{2+}$and $NH_3^{2+}$) were calculated using the Gaussian 03 program and Gaussian 2 calculations. Then, the adiabatic double ionization energies of the molecules were predicated by using high accuracy energy mode. The experimental double ionization energies of these small molecules were all in reasonable agreement with their respective calculated adiabatic double ionization energies. The mechanisms of double photoionization of these molecules were discussed based on a comparison of our experimental results with those predicted theoretically. The equilibrium geometries and harmonic vibrational frequencies of molecules and their parent dications were calculated by using the MP2 (full) method. The differences in configurations between these molecules and their parent dications were also discussed on the basis of theoretical calculations.

**Keywords:** double photoionization, synchrotron radiation, dication, adiabatic double ionization energy

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## 1. Introduction

Doubly charged molecular ions or dications have been widely studied over recent decades, due to their unusual nature. Molecular ions with two positive charges or molecular dications, such as $CO_2^{2+}$, are usually intrinsically unstable and easy to dissociate into two singly charged fragment ions, because the Coulombic repulsion between the positive charges dominates the long range interaction of two fragments from molecular dication. Stable and metastable molecular dications are still observed because at short range covalent bonding can overcome these repulsive Coulombic forces within the molecule. The stabilities of these molecular dications are determined by the interaction between these forces. The forces are finally balanced in metastable states where molecular dications are stable for nanoseconds or longer and then become fragments.[1]

Doubly charged dications can be formed in double photoionization via the simplified schemes depicted in the following equations for a diatomic molecule AB:

$$\mathrm{AB}+h\nu \rightarrow \begin{cases} \mathrm{AB}^{2+}+2\mathrm{e}, & (1)\\ \mathrm{A}^{2+}+\mathrm{B}+2\mathrm{e}, & (2)\\ \mathrm{A}+\mathrm{B}^{2+}+2\mathrm{e}, & (3)\\ \mathrm{A}^{+}+\mathrm{B}^{+}+2\mathrm{e}, & (4) \end{cases}$$

Of course, many more reaction pathways are possible for the double photoionization of diatomic or polyatomic molecule, but the basic double ionization schemes involve parent dication formation (equation (1)) and fragment dication formation (equation (2) or (3)) as well as the ion-pair formation process (equation (4)).

There are lots of methods to investigate dou-

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bly charged dications of these small molecules, such as the photoion–photoion coincidence (PIPICO) technique,[2−6] photoelectron–photoion–photoion coincidence (PEPIPICO) spectra,[7−8] photoionization mass spectrometry (PIMS),[9] Auger spectroscopy (AS),[10−14] translational energy spectroscopy (TES),[15] double-charge-transfer spectroscopy (DCTS),[5,16−19] photoion–photon of fluorescence coincidence measurements (PIFCO),[20] threshold photoelectrons coincidence spectrum (TPEsCO),[21−23] time-of-flight photoelectron–photoelectron coincidence (TOF–PEPECO),[1,24−26] electron impact mass spectroscopy (EIMS),[27−35] and theoretical calculations.[5,18,25,36−47] Recently, the intense femtosecond laser fields have been used to investigate double ionization of small molecules.[48−50] Those published investigations mainly focused on double ionization cross sections, electronic states of dications, double ionization threshold, dissociation of dications, autoionization of atomic fragment, the kinetic-energy release (KER) and angular distribution in the dissociation of doubly charged molecular parent dications. Even so, the mechanisms of double ionization of these small molecules are still less well understood in detail experimentally and theoretically, especially for their double ionization thresholds.

In this paper, we present a study of VUV double photoionization of molecules using photoionization mass spectroscopy (PIMS). The double ionization energies (DIE) $E_{\rm DIE}$ of molecules were determined with photoionization efficiency spectroscopy (PIES). The theoretical $E_{\rm DIE}$ of molecules were predicted by using quantum chemistry calculations, which were performed using the Gaussian-03 program and G2 method to obtain some photochemical parameters. Then, the mechanisms of adiabatic double photoionization of molecules were discussed. The geometries and vibrational frequencies of these molecules and their parent dications were also calculated by using the MP2 (full) method.

## 2. Experimental

The experimental apparatus has been described elsewhere.[51−53] In brief, the experiment was carried out at the Atomic and Molecular Physics Beamline U14-A Station of the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The synchrotron radiation beam from an Undulator of the 800-MeV electron storage ring of the NSRL is monochromatized with a 6-m length monochromator equipped with three gratings (1250, 740 and 370 lines/mm). The 740 lines/mm grating covers the energy range from 15 eV to 45 eV, and its resolving power ($E/\Delta E$) is about 1000 $\sim$ 5000, depending on the widths of the entrance and exit slits. Usually, these two silts are both adjusted to a 80-μm width with a resolving power of 3200 at 28.962 eV. The average photon flux was measured to be about $5\times10^{12}$ photons/s. The monochromatized synchrotron radiation was focused by a toroidal mirror into the photoionization chamber. In this experiment, the wavelength of the monochromator was calibrated with the known ionization energies and special ionization spectra of inert gases (He, Ne, Ar).

The samples were introduced by supersonic expansion through a continuous beam nozzle with an orifice of 70-μm diameter from the molecular beam chamber into the ionization chamber through a $\phi$1 mm skimmer. The molecular beam intersected the monochromatized synchrotron radiation beam at 70 mm from the nozzle. A reflectron time-of-flight mass spectrometer (RTOFMS) was employed for the VUV photoionization studies. Photoions produced by the VUV light were drawn out of the photoionization region by a pulse extraction field triggered by a pulse generator (DG 535 SRS) and detected by a microchannel plate (MCP) detector. The photoion signals from the detector were counted with a multiscaler P7888 counter (FAST Comtec, Germany) after they were amplified with a preamplifier VT120C (EG & G, ORTEC) and transferred to a computer for further processing. The PIMS spectrum of the molecule can be obtained when it is excited by using a fixed photon energy above its ionization threshold.

In this experiment, the pressure of the ionization chamber was about $1\times10^{-3}$ Pa when the molecular beam was introduced, while the stagnation pressure was about 0.1 MPa. The PIES curve was measured while the monochromator was scanned with an energy increment of 10 meV, and the data acquisition time for each point was 20 s, depending on the ion abundance. To normalize the ion signals, the photon intensity was monitored simultaneously with a silicon photodiode (SXUV-100, International Radiation Detectors, Inc.).

## 3. Quantum chemical calculations

The total energies of the molecules and their parent dications were calculated with the Gaussian-03 program and G2 method.[54−56] In brief, the equilibrium structure of the molecule was optimized and its harmonic vibrational frequencies were calculated at first by HF/6-31G(d). Its zero point energy was timed by a factor of 0.8929. Then the equilibrium structure of the molecule was optimized again at MP2 (Full)/6-31G* level. To calculate an $E_0$(G2) energy, zero-point energy calculations were carried out at the levels of MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-311G(2df,p), MP2/6-311+G(3df,2p), and QSCISD(T)/6-311G(d,p) with a higher-level correction and a zero-point vibrational energy correction. After the calculation of the energy $E_0$(G2), the high accuracy energy model was used to calculate the adiabatic $E_{\rm DIE}$ of the molecule. According to the theory, the adiabatic $E_{\rm DIE}$ refers to the energy difference ($\Delta E$) between two zero-point energies of a neutral molecule and its parent dication at their respective optimized geometries, while the calculated value is simply $\Delta E$ between two energy minima.[40] In this study, the adiabatic $E_{\rm DIE}$ is calculated as the energy difference ($\Delta E$) between the total energy of

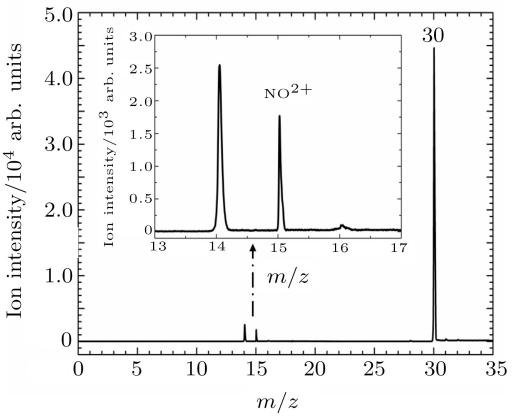



**Fig. 1.** Photoionization mass spectra of NO at the photon energy of 45 eV.

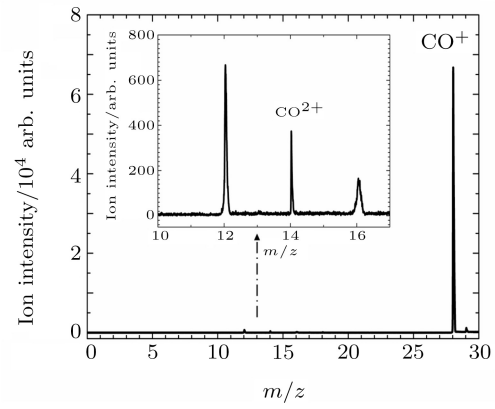



**Fig. 2.** Photoionization mass spectra of CO at the photon energy of 45 eV.

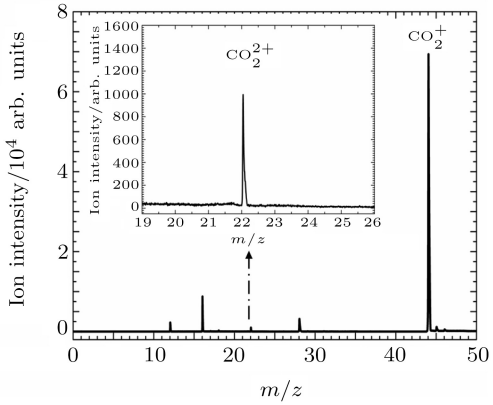



**Fig. 3.** Photoionization mass spectra of $CO_2$ at the photon energy of 45 eV.

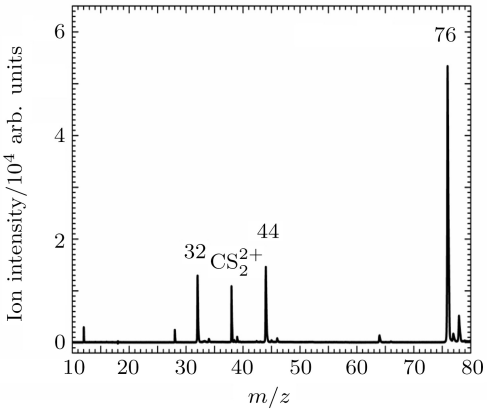



**Fig. 4.** Photoionization mass spectra of $CS_2$ at the photon energy of 40 eV.

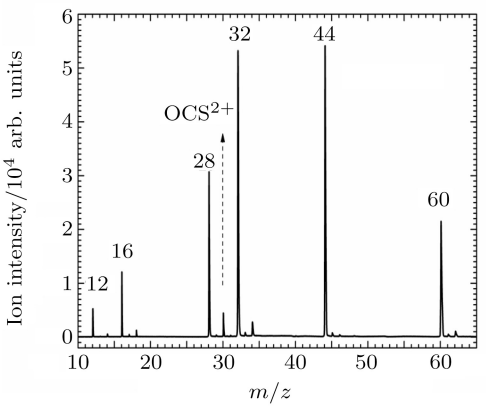



**Fig. 5.** Photoionization mass spectra of OCS at the photon energy of 38 eV.

the neutral molecule and that of the parent dication in their respective lowest electronic states. The equilibrium geometries and vibrational frequencies of molecules and their parent dications were calculated by using the 6-31G(d) basis sets at the MP2 (full) levels of theory.

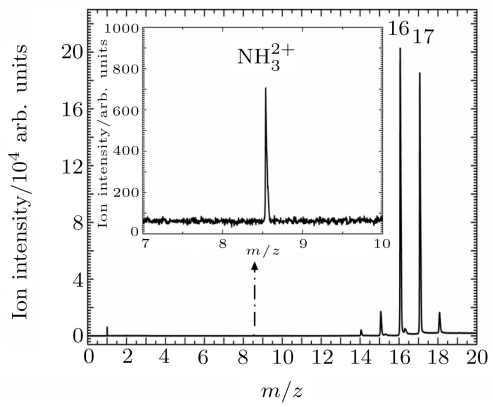



**Fig. 6.** Photoionization mass spectra of $NH_3$ at the photon energy of 45 eV.

# 4. Results and discussion

## 4.1. PIMS and PIES

The PIMS curves of these small molecules (NO, CO, $CO_2$, $CS_2$, OSC and $NH_3$) at their respective higher photon energies are shown in Figs. 1–6, respectively. Besides the singly charged parent ions and all fragment ions, the doubly charged parent dications ($NO^{2+}$, $CO^{2+}$, $CO_2^{2+}$, $CS_2^{2+}$, $OSC^{2+}$and $NH_3^{2+}$) are all observed in this experiment. From these figures, we can find that the intensities of these dications signals are quite weak, mainly because their lifetimes are very short due to the Coulombic repulsion for dication with two positive charges. By the way, there is an ion signal ($m/z = 28$) in Fig. 4 that is $N_2^+$.

The PIES curves of these molecular parent dications in the photon energy ranges from their respective double ionization thresholds to higher energies were recorded at a scan step of 10 meV, and normalized with respect to the photon flux. As examples, the PIES curves of dications ($NO^{2+}$, $CO^{2+}$, $CO_2^{2+}$) are shown in Figs. 7–9, respectively. In the study of SRVUV double photoionization of these molecules, their $E_{\rm DIE}$ can be obtained directly by scanning the wavelength of the monochromatized synchrotron radiation. It should be pointed out that we ignored the thermal energy distribution of these parent molecules in our data processing, considering the present nozzle expansion condition mentioned above.

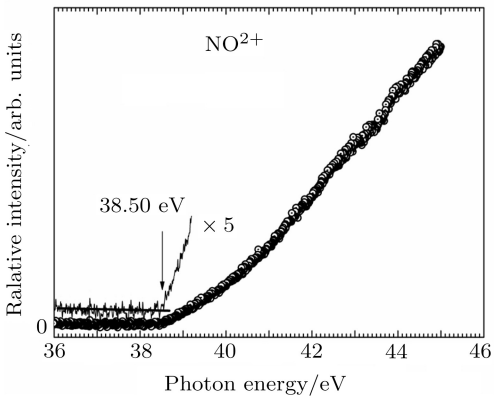



**Fig. 7.** Photoionization efficiency spectroscopy curve of $NO^{2+}$.

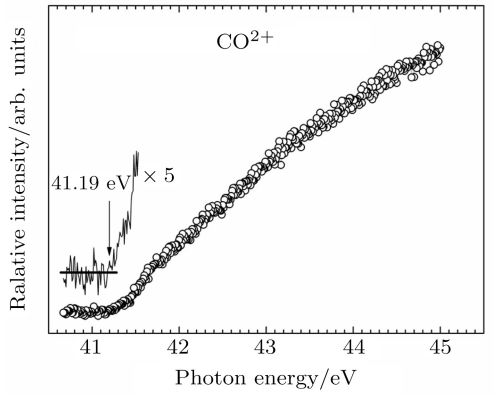



**Fig. 8.** Photoionization efficiency spectroscopy curve of $CO^{2+}$.

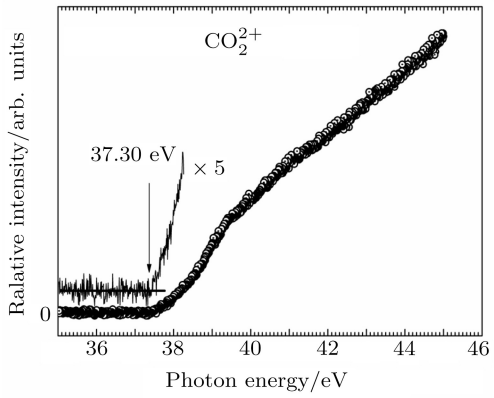



**Fig. 9.** Photoionization efficiency spectroscopy curve of $CO_2^{2+}$.

From the PIES curves of these parent dications, the onsets of double photoionization of $NO^{2+}$ (Fig. 7), $CO^{2+}$ (Fig. 8), $CO_2^{2+}$ (Fig. 9), $CS_2^{2+}$ (Fig. 10), $OSC^{2+}$ (Fig. 11) and $NH_3^{2+}$(Fig. 12) are $38.50 \pm 0.01$, $41.19 \pm 0.01$, $37.30 \pm 0.02$, $27.05 \pm 0.01$, $30.25 \pm 0.02$ and $33.42 \pm 0.03$ eV, respectively, as listed in Table 1.

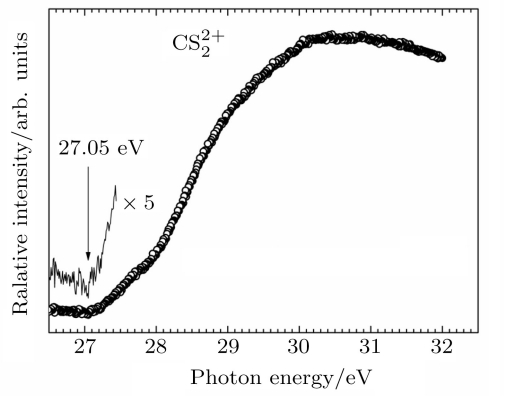



**Fig. 10.** Photoionization efficiency spectroscopy curve of $CS_2^{2+}$.

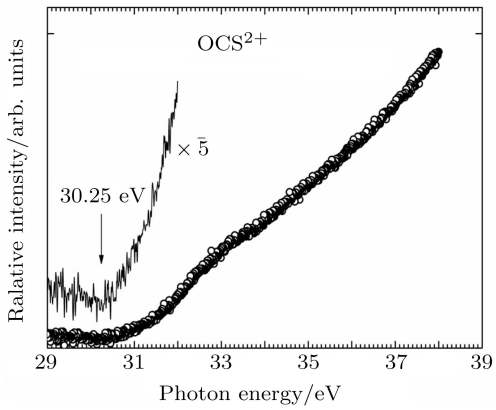



**Fig. 11.** Photoionization efficiency spectroscopy curve of $OCS^{2+}$.

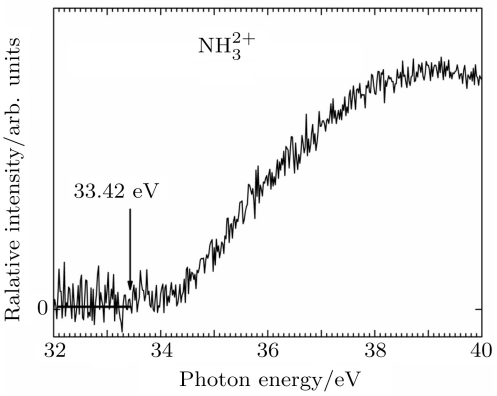



**Fig. 12.** Photoionization efficiency spectroscopy curve of $NH_3^{2+}$.

## 4.2. Results of calculations

### 4.2.1. Double ionization energies

In this study, total energies $E_0$(G2) of these molecules and their parent dications were calculated at first with the Gaussian 03 program and G2 method. The total energies of these molecules and their parent dications are given in Table 2. In the high accuracy energy model of Gaussian 03, the adiabatic $E_{\rm DIE}$ of the molecule is taken as the amount of energy required to remove two electrons from a neutral molecule, computed as the total energy difference ($\Delta E_0$(G2)) between the neutral molecule and its parent dication in their respective lowest states. For example, the adiabatic $E_{\rm DIE}$ of CO is calculated as follows,

$$\begin{aligned} E_{\rm DIE}({\rm CO}) &= E_0({\rm G2})({\rm CO}^{2+}, X^3\Pi) - E_0({\rm G2})({\rm CO}, X^1\Sigma) \\ &= (-111.661359) - (-113.175409)\ \text{Hartree} \\ &= 41.199\ \text{eV}. \end{aligned}$$

This theoretical value of adiabatic $E_{\rm DIE}$ of CO is in very good agreement with our experimental one of 41.19±0.01 eV. The adiabatic $E_{\rm DIE}$ of other molecules can also be calculated in the same way. These are given in Table 1.

**Table 1.** Experimental, theoretical and literature values of the double ionization energy (DIE).

| molecules | this work $E_{\rm DIE}$/eV | | literature | | | |
|---|---|---|---|---|---|---|
| | experimental (MS–PIES) | theoretical (G2) | experimental $E_{\rm DIE}$/eV | Ref. | theoretical $E_{\rm DIE}$/eV | Ref. |
| NO | 38.50 ± 0.01 | 38.490 | 38.476 ± 0.01 (TPEsCO) | [21] | | |
| | | | 38.446 ± 0.01 (TOF–PEPECO) | [24] | 38.47 (PEC) | [39], [41] |
| | | | 38.5 ± 0.1 (PIPICO) | [3] | 38.71 (DFT) | [40] |
| | | | 39.3 ± 0.3 (EIMS) | [27] | | |
| | | | 39.5 ± 0.3 (EIMS) | [28] | | |
| | | | 39.8 ± 0.3 (EIMS) | [29] | | |

**Table 1.** (*Continued*)

| molecules | this work $E_{\rm DIE}$/eV | | literature | | | |
|---|---|---|---|---|---|---|
| | experimental (MS–PIES) | theoretical (G2) | experimental $E_{\rm DIE}$/eV | Ref. | theoretical $E_{\rm DIE}$/eV | Ref. |
| CO | $41.19 \pm 0.01$ | 41.199 | $41.294 \pm 0.01$ (TPEsCO) | [21] | 41.290 (PEC) | [42] |
| | | | $41.3 \pm 0.3$ (PIPICO) | [4] | 42.13 (DFT) | [40] |
| | | | $41.8 \pm 0.3$ (EIMS) | [29] | | |
| | | | $41.8 \pm 0.5$ (EIMS) | [30] | | |
| $CO_2$ | $37.30 \pm 0.02$ | 37.124 | $37.340 \pm 0.01$ (TOF–PEPECO) | [1] | 37.58 (MP2) | [36] |
| | | | $37.2 \pm 0.1$ (TPEsCO) | [22] | 37.65 (DFT) | [40] |
| | | | $38.0 \pm 0.2$ (EIMS) | [31] | | |
| $CS_2$ | $27.05 \pm 0.01$ | 26.917 | $27.05 \pm 0.01$ (TPEsCO) | [23] | 26.87 (MP2) | [36] |
| | | | $27.0 \pm 0.3$ (PEPIPICO) | [8] | 27.08 (DFT) | [40] |
| | | | $27.4 \pm 0.2$ (EIMS) | [31] | | |
| OSC | $30.25 \pm 0.02$ | 29.910 | $30.10 \pm 0.01$ (TOF–PEPECO) | [25] | 30.05 (MRCI) | [25] |
| | | | $31.8 \pm 0.5$ (EIMS) | [32] | 30.74 (DFT) | [40] |
| $NH_3$ | $33.42 \pm 0.03$ | 33.438 | $33.4 \pm 0.1$ (TOF–PEPECO) | [26] | 33.68 (SCF) | [18] |
| | | | $34.4 \pm 0.2$ (EIMS) | [35] | 34.51 (CI) | [18] |

Note: The values quoted from Ref. [40] are vertical $E_{\rm DIE}$ calculated with DFT.

**Table 2.** Total G2 energies of molecules and their parent dications.

| molecules | state | $E_0$(G2)/Hartree | dications | state | $E_0$(G2)/Hartree |
|---|---|---|---|---|---|
| NO | D | −129.736221 | $NO^{2+}$ | D | −128.321713 |
| CO | S | −113.175409 | $CO^{2+}$ | T | −111.661359 |
| $CO_2$ | S | −188.356615 | $CO_2^{2+}$ | T | −186.987317 |
| $CS_2$ | S | −833.521652 | $CS_2^{2+}$ | T | −832.532446 |
| OCS | S | −510.939547 | $OSC^{2+}$ | T | −509.84031 |
| $NH_3$ | S | −56.457174 | $NH_3^{2+}$ | S | −55.228340 |

### 4.2.2. Geometries and vibrational frequencies

The geometries of these molecules and their parent dications were optimized by using the MP2 (full) method in conjunction with the 6–31G(d) basis sets, as implemented in the Gaussian 03 program suite. The vibrational frequencies of these molecules and their parent dications were calculated by the geometry optimizations, as described above. The optimized parameters, such as the bond lengths, bond angles and vibrational frequencies, are given in Table 3.

**Table 3.** The calculated (MP2 (Full)/6–31G (d)) bond lengths (Å, 1 Å = 0.1 nm), bond angles (degrees) and vibrational frequencies ($cm^{-1}$) for molecules and their parent dications.

| molecules | | bond length/Å | | bond angle/(°) | vibrational frequency/$cm^{-1}$ | |
|---|---|---|---|---|---|---|
| NO | neutral | N–O | 1.1427 | – | 3895.2529 | |
| | dication | | 1.0314 | – | 2782.3667 | |
| CO | neutral | C–O | 1.1502 | – | 2124.5783 | |
| | dication | | 1.2414 | – | 1545.4786 | |
| $CO_2$ | neutral | O–C–O | 1.1786 | 180 | 641.9896 | 641.9896 |
| | | | 1.1786 | | 1336.4694 | 2454.6000 |
| | dication | | 1.1977 | 180 | 463.8938 | 463.8938 |
| | | | 1.1977 | | 1234.5313 | −1178.6792 |

**Table 3.** (*Continued*)

| molecules | | bond length/Å | | bond angle/(°) | vibrational frequency/cm$^{-1}$ | |
|---|---|---|---|---|---|---|
| $CS_2$ | neutral | S–C–S | 1.5613 | 180 | 402.4321 | 402.4321 |
| | | | 1.5613 | | 686.3396 | 1643.4775 |
| | dication | | 1.5605 | 180 | 338.0450 | 338.0450 |
| | | | 1.5605 | | 643.5250 | 688.1064 |
| OCS | neutral | O–C–S | 1.1787 | 180 | 502.4221 | 502.4221 |
| | | | 1.5648 | | 902.8018 | 2117.4101 |
| | dication | | 1.0966 | 180 | 403.1958 | 403.1958 |
| | | | 1.8631 | | 542.1917 | 3805.1803 |
| | | | 1.0168 | 106.3579 | 1755.6342 | 1755.6342 |
| $NH_3$ | neutral | N–H | 1.0168 | 106.3579 | 1160.6132 | 3504.3438 |
| | | | 1.0168 | 106.3579 | 3660.4716 | 3660.4716 |
| | | | 1.1003 | 120.0 | 1402.6336 | 1402.6336 |
| | dication | | 1.1003 | 120.0 | 1535.2149 | 2725.0853 |
| | | | 1.1003 | 120.0 | 2775.5847 | 2775.5847 |

## 4.3. Discussion

### 4.3.1. $NO^{2+}/NO$

Previous investigations of the doubly charged dications $NO^{2+}$ include PIPICO, PIMS, AS, TES, DCTS, PIFCO, TOF–PEPECO, TPEsCO, EIMS, and theoretical calculations.[2,3,9,10,15,16,20,21,24,27,28,37,38] The theoretical $E_{\rm DIE}$ of NO ranges from 35.1 eV to 39.8 eV[28] and the closest approximation to date seems to be $(38.6 \pm 0.1)$ eV.[3,20,39]

The experimental $E_{\rm DIE}$ of NO is (38.50±0.01) eV, which is in very good agreement with the theoretical value, 38.490 eV, predicted by quantum chemical calculations. The value of $(38.50 \pm 0.01)$ eV is also in reasonable agreement with the energies of $(38.476 \pm 0.01)$ eV determined by using TPEsCO,[21] $(38.46 \pm 0.01)$ eV determined by using TOF–PEPECO,[24] and $(38.5 \pm 0.1)$ eV determined by using PIPICO.[3] Our theoretical value of adiabatic $E_{\rm DIE}$ of NO, 38.490 eV, is in good accordance with that one, 38.470 eV, calculated by using potential energy curves (PEC),[39,41] but less than the vertical one 38.71 eV calculated by Chong using density functional theory (DFT).[40]

In the studies of EIMS performed by Kim *et al.*, Wetmore *et al.* and Dorman *et al.*,[27–29] the $E_{\rm DIE}$ of NO are $(39.3 \pm 0.3)$, $(39.5 \pm 0.3)$, and $(39.8 \pm 0.3)$ eV, respectively, which are greater than ours. The poor agreement of our experimental $E_{\rm DIE}$ of NO with those ones in EIMS can be explained as follows. A fundamental and important difference exists between photon impact ionization and electron impact ionization. A photon is annihilated in such an event whereas an electron is not; it is scattered with a lower energy than it had before its impact. Since a photon must be annihilated in the process of single photon excitation, the double ionization by photon impact is a resonance process that occurs when $h\nu = E_{\rm DIE}$, unlike the electron impact situation where the primary electron energy $E_{\rm p} > E_{\rm DIE}$. The double ionization by electron impact and double ionization by photon impact are also rather different phenomena, and they go by different threshold ionization laws. An obvious practical consequence of the differences in the threshold law is that accurate double ionization is more easily obtainable from photon impact double ionization efficiency curves than that from the corresponding electron impact curves.[57] Another reason for these differences is the inherent lack of resolution in most electron impact apparatus. From the above discussion, our experimental value, $(38.50 \pm 0.01)$ eV, is reasonable and should be adiabatic $E_{\rm DIE}$ of NO.

NO is an open shell molecule, and its electronic configuration is given by $(1\sigma)^2\ (2\sigma)^2\ (3\sigma)^2\ (4\sigma)^2\ (1\pi)^4\ (5\sigma)^2\ (2\pi)^1$. The present calculations show that the lowest energy of $NO^{2+}$ occurs for a duplet state ($X^2\Sigma$), and its outmost valence electronic configuration is given by $(3\sigma)^2\ (4\sigma)^2\ (1\pi)^4\ (5\sigma)^1$. The equilibrium bond lengths and vibrational frequencies of the lowest states NO ($X^2\Sigma$) and $NO^{2+}$ ($X^2\Sigma$) are shown in Table 3. The equilibrium bond length (N–O) of $NO^{2+}$ ($X^2\Sigma$) is shorter than that of NO ($X^2\Sigma$), which is in accordance with calculations by Thulstrup *et al.*[37]

#### 4.3.2. $CO^{2+}/CO$

There are lots of methods to investigate doubly charged dications of $CO^{2+}$, such as PIMS, EIMS, AS, TES, DCTS, PIFCO, PIPICO, TOF–PEPECO, TPEsCO and theoretical calculations, etc. Although the $E_{DIE}$ of CO, as described in the current literature, ranges from 39.5 eV to 41.8 eV, the closet approximation to date seems to be about $(41.4 \pm 0.4)$ eV.[17]

The experimental $E_{DIE}$ of CO is (41.19±0.01) eV, which is in extraordinary agreement with our theoretical value, 41.199 eV, and also with the energies of $(41.294 \pm 0.01)$ eV determined by using TPEsCO,[21] and $(41.3 \pm 0.3)$ eV determined by using PIPICO.[4] Our theoretical value of 41.199 eV is close to that one, 41.290 eV, calculated by using PEC,[42] but less than the vertical one, 42.13 eV calculated by Chong.[40] By discussion in the same way as mentioned above, our value obtained in this experiment is reasonable and in very good agreement with theoretical adiabatic $E_{DIE}$ of CO.

CO is a close shell molecule, and its valence electronic configuration is given by $(4\sigma)^2\ (1\pi)^4\ (5\sigma)^2$. The present calculations show that the lowest energy of $CO^{2+}$ occurs for a triplet state ($X^3\Pi$), which is in agreement with that calculated by Larsson *et al.*[43]and with that measured by Dawber *et al.*[21] The equilibrium bond length and vibrational frequency of the lowest states CO ($X^1\Sigma$) and $CO^{2+}$ ($X^3\Pi$) are shown in Table 3. The equilibrium bond length (C–O) of $CO^{2+}$ is longer than that of CO, which is in accordance with calculations by Wetmore *et al.*[44]

#### 4.3.3. $CO_2^{2+}/CO_2$

The $CO_2^{2+}$ dication has frequently been studied experimentally since it was first observed in 1961.[29]

Various methods, such as PIMS, EIMS, DCTS, AS, TOF–PEPECO and TPEsCO, etc., have been designed to study its appearance energy.

The experimental $E_{DIE}$ of $CO_2$ is $(37.30 \pm 0.02)$ eV, which is in reasonable agreement with our theoretical value, 37.124 eV. The value of $(37.30 \pm 0.02)$ eV is also in accordance with those ones of $(37.34 \pm 0.01)$ eV determined by using TOF–PEPECO[1] and $(37.2 \pm 0.1)$ eV determined by using TPEsCO.[22] Our theoretical value, 37.124 eV, is less than the vertical $E_{DIE}$, 37.65 eV, calculated by Chong.[40] In the same way as we discussed above, our experimental $E_{DIE}$ of $CO_2$ is reasonable and in agreement with the theoretical adiabatic one.

The outermost orbits of $CO_2$ in order of energy are $(4\sigma_g)^2\ (3\sigma_u)^2\ (1\pi_u)^4\ (1\pi_g)^4$. By calculation, the lowest energy of $CO_2^{2+}$ occurs for a triplet state ($X^3\Sigma_g^-$), which is in accordance with that calculated by Millie *et al.* and Hochlaf *et al.*[5,45] and with that measured by Slattery *et al.*[1] From Table 3, we can find that the equilibrium bond lengths (C–O) in the lowest state of $CO_2^{2+}$ ($X^3\Sigma_g^-$) are longer than that in the lowest state $CO_2$ ($X^1\Sigma_g^+$), which is in agreement with calculations by Hochlaf *et al.*[45]

#### 4.3.4. $CS_2^{2+}/CS_2$

The doubly charged dication $CS_2^{2+}$ was first observed with EIMS in 1964.[33] Many theoretical and experimental studies have been carried out for this dication. Experimentally, PIPICO experiment has located the double ionization threshold of $CS_2$ at about $(27.2 \pm 0.2)$ eV.[5]

The experimental $E_{DIE}$ of $CS_2$ is (27.05±0.01) eV, which is in good agreement with our calculated theoretical one, 26.917 eV. The value of $(27.05 \pm 0.01)$ eV is also in very good accordance with the energies of $(27.05 \pm 0.01)$ eV determined by using TPEsCO[23] and (27.0±0.3) eV determined by using PEPIPICO.[8] By discussion in similar ways as mentioned above, our experimental $E_{DIE}$ of $CS_2$ is reasonable and in good accordance with the theoretical adiabatic one.

The outermost orbits of $CS_2$ in order of energy are $(6\sigma_g)^2\ (5\sigma_u)^2\ (2\pi_u)^4\ (2\pi_g)^4$. By calculation, the lowest energy of $CS_2^{2+}$ occurs for a triplet state ($X^3\Sigma_g^-$), which is in accordance with calculations by Millie *et al.*[5] and Taylor *et al.*[46] and with that measured by Hochlaf *et al.*[23] From Table 3, we can find that there is only a small difference in the equilibrium bond lengths (C–S) from the lowest state $CS_2$ ($X^1\Sigma_g^+$) to $CS_2^{2+}$ ($X^3\Sigma_g^-$), which is in good agreement with that calculated by Taylor *et al.*[46]

#### 4.3.5. $OCS^{2+}/OCS$

For the dication $OCS^{2+}$, the pattern of electronic states was determined using EIMS, (DCT), (PIPICO), TPEsCO, AS and TOF–PEPECO.[5,6,11,22,32] Theoretically, the spectrum of the electronic states of $OCS^{2+}$ was first computed by Millie *et al.*[5] by using an SCF-CI treatment.

The experimental $E_{DIE}$ of OCS is $(30.25 \pm 0.02)$ eV, which is in agreement with our calculated theoretical one, 29.91 eV. The value of

$(30.25 \pm 0.02)$ eV is also in accordance with the energy of $(30.1 \pm 0.5)$ eV determined by using TOF–PEPECO.[25] From the similar discussion above, our value obtained in this experiment is reasonable and close to theoretical adiabatic $E_{\rm DIE}$ of OCS.

The outermost orbits of OCS in order of energy are $(6\sigma)^2$ $(5\sigma)^2$ $(1\pi)^4$ $(2\pi)^4$. By our calculations, the lowest energy of $OCS^{2+}$ occurs for a triplet state $(X^3\Sigma^-)$, which is in accordance with calculations by Millie *et al.*[5] and Brites *et al.*[25] The equilibrium bond lengths, bond angles and vibrational frequencies of the lowest states OCS $(X^1\Sigma^+)$ and $OCS^{2+}$ $(X^3\Sigma^-)$ are shown in Table 3. The equilibrium bond length (C–O) becomes shorter in the dication, and in contrast to the $OCS^{2+}$ bond length (C–S) it becomes longer by double ionizing OCS, which is in agreement with those calculations.[25] The C–O and C–S bond lengths in dications $OCS^{2+}$ $(X^3\Sigma^-)$ are 1.0966 Å and 1.8631 Å, respectively, which are also close to 1.11 Å and 1.79 Å calculated by Brites *et al.*[25]

#### 4.3.6. $NH_3^{2+}$/ $NH_3$

Doubly charged dication $NH_3^{2+}$ has been studied with calculations, EIMS, AS, DCTS and TOF–PEPECO previously.[12−14,18,19,26,35,47] Vertical double ionization produces significant amounts of metastable dication $NH_3^{2+}$ with an onset at about 34 eV.[35] The majority of the nascent doubly charged ions are easy to dissociate into ion pairs with a considerable kinetic energy release.[58]

In our study of PIES curve of dication $NH_3^{2+}$ (Fig. 12), the change in geometry on double ionization results in a very gradual onset for the first double ionization band. Probably the Franck–Condon factor of (0–0) transition is very small. Therefore, it is not easy to obtain adiabatic $E_{\rm DIE}$ from our spectra. From the PIES curve of $NH_3^{2+}$, we can find there is a weak onset at $(33.42 \pm 0.03)$ eV which is in agreement with our theoretical value of 33.438 eV and also close to the energy of $(33.4 \pm 0.1)$ eV determined by using TOF–PEPECO.[26] By discussion in a similar way as above, our experimental $E_{\rm DIE}$ of $NH_3$ is rational and in accordance with the theoretical adiabatic one.

The electronic configuration of $NH_3$ is $(1a_1)^2$ $(2a_1)^2$ $(1e)^2$ $(3a_1)^2$, in its ground state the molecule $NH_3$ is pyramidal ($C_{3\nu}$ symmetry group). By calculation, the lowest energy of $NH_3^{2+}$ occurs for a singlet state $(X^1A_1)$, also being pyramidal ($C_{3\nu}$ symmetry group), which is in accordance with those calculations.[18] The bond lengths, bond angles and vibrational frequencies of the lowest states $NH_3$ $(X^1A_1)$ and $NH_3^{2+}$ $(X^1A_1)$ are shown in Table 3. The N–H bond length of $NH_3^{2+}$ $(X^1A_1)$ is longer than that of $NH_3$ $(X^1A_1)$, and the H–N–H bond angle of $NH_3^{2+}$ $(X^1A_1)$ is larger than that of $NH_3$ $(X^1A_1)$. The N–H bond length of $NH_3^{2+}$ is 1.0168 Å, which is close to 1.911 a.u. calculated by Appell *et al.*[18]

## 5. Conclusions

Double ionization energies of small molecules (NO, CO, $CO_2$, $CS_2$, OSC and $NH_3$) have been obtained from experimental studies of double photoionization by using synchrotron radiation, photoionization mass spectroscopy, and photoionization efficiency spectroscopy. The total energies of molecules and their parent dications were calculated by using the Gaussian 03 program and G2 method. Then their adiabatic double ionization energies were estimated using these total energies. Generally speaking, the experimental double photoionization energies of these small molecules are reasonable and in good agreement with their respective theoretical adiabatic double ionization energies. On the basis of the comparison between experimental results and those of theoretical calculations, the mechanisms of double photoionization of these small molecules are discussed. The differences i bond lengths, bond angles and vibrational frequencies between molecules and their respective parent dications were also discussed based on a comparison between our theoretical calculations and the literature.

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