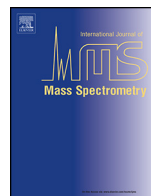




Contents lists available at ScienceDirect

## International Journal of Mass Spectrometry

journal homepage: [www.elsevier.com/locate/ijms](http://www.elsevier.com/locate/ijms)

## High resolution low-energy electron attachment to molecular clusters of sulfur dioxide

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## ARTICLE INFO

## Article history:

Received 29 November 2013

Received in revised form

30 December 2013

Accepted 31 December 2013

Available online xxx

## Keywords:

Electron attachment

Sulfur dioxide clusters

Anion formation

Cross sections

Vibrational Feshbach resonances

## PACS:

34.80.Lx

34.80.Ht

34.80.Qb

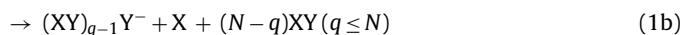
## ABSTRACT

Using the laser photoelectron attachment method, we have investigated the formation of cluster anions in low-energy free electron attachment ( $E = 1\text{--}200$  meV) as well as in Rydberg electron transfer (at principal quantum numbers 20–260) to molecular clusters of sulfur dioxide ( $\text{SO}_2$ ) in a collimated supersonic beam at high electron energy resolution (energy width  $\leq 2$  meV). At these low energies (almost) only homogeneous cluster anions  $(\text{SO}_2)_q^-$  ( $q \geq 1$ ) are found with energy dependences which show – superimposed on a monotonically decreasing continuum cross section – characteristic peaks which are interpreted as vibrational Feshbach resonances (VFR), associated with excitation of the three fundamental vibrational modes in the  $\text{SO}_2$  molecule, namely bending (010), symmetric stretch (100), and asymmetric stretch (001). The VFRs are clear for  $q = 2\text{--}12$ , but only weak for  $q = 1$ . The energy positions of the VFRs are progressively red-shifted with increasing cluster anion size  $q$  by about 1.7 meV per added molecular unit, and the peaks broaden towards larger  $q$ . The cross section enhancement in the VFRs – compared to the size of the continuum – is substantial, indicating that the VFRs act as important doorway states for electron capture. Model  $R$ -matrix calculations are presented which recover the main features of the experimental attachment spectra for cluster anion formation and suggest that VFRs occur for neutral  $(\text{SO}_2)_N$  clusters with sizes  $N \geq 4$ . With growing  $N$ , the electron binding energy increases and the capture cross section decreases. In contrast, the Vogt–Wannier model for electron capture into a polarization well predicts a growth of the cross section with the cluster size.

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## 1. Introduction

Transient negative ion states  $(XY)_N^{-*}$  are known to be crucial for vibrational excitation [1–3] and negative ion formation [1–5] in low-energy electron collisions with molecules  $XY$  ( $N = 1$ ) and molecular clusters  $(XY)_N$  ( $N \geq 2$ ) (described by a set of quantum numbers  $\{\alpha\}$  denoting their electronic and ro-vibrational state):



Here path (1a) describes elastic ( $\alpha = \alpha'$ ) or inelastic scattering. Process (1b) represents dissociative electron attachment (DEA) while in the reaction (1c) (only relevant for clusters, i.e.  $N \geq 2$ ) anion formation proceeds through evaporation of  $XY$  constituents. Even if no other stabilizing process occurs, the temporary negative ion  $(XY)_N^{-*}$  ( $N \geq 1$ ) can become metastable with respect to spontaneous re-emission (autodetachment) of the electron, if the electronic energy is rapidly redistributed into internal degrees of freedom (intra- and intermolecular vibration, rotation), thereby yielding long-lived negative ions  $(XY)_N^{-\ddagger}$  in path (1d). We note that targets of molecular clusters  $(XY)_N$ , created in supersonic beams, typically contain a broad distribution of sizes  $N$ . As a consequence, the correlation of the observed anion cluster size  $q$  with the size  $N$  of the neutral cluster precursor relevant for the reactions (1b), (1c) is not *a priori* known.

Clusters serve as nanoscale objects for studying the effects of solvation due to the interaction between a solvated molecule or ion and its surrounding solvent environment. Solvation effects also play a key role in the formation of negative ions by attachment of slow electrons to molecular clusters [4–8]. The anion resonances, observed for single molecules, appear shifted towards lower energies in clusters due to the effects of solvation [4–8]. An intriguing

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result in early studies of cluster anion formation was the observation of a prominent peak at near-zero energy in cases where such a feature is absent in the monomer [4,7–9] (e.g. for clusters of CO<sub>2</sub>, N<sub>2</sub>O, and H<sub>2</sub>O), but the true nature of this ‘zero energy resonance’ [4,8] remained uncertain for some time.

Using the laser photoelectron attachment (LPA) method at energy widths around 1 meV [3], our group demonstrated that the cluster anion yield in low-energy (0–200 meV) electron collisions with clusters of XY = N<sub>2</sub>O [10,11], and CO<sub>2</sub> [12,13] is to a large extent mediated by narrow vibrational Feshbach resonances (VFRs) [3,14], i.e. temporary negative ion states of the type [(XY)<sub>N-1</sub>XY( $\nu_i \geq 1$ )]<sup>-</sup> which occur at energies below those of the neutral cluster [(XY)<sub>N-1</sub>XY( $\nu_i \geq 1$ )] (here the vibrational excitation  $\nu_i$  in the VFR and the neutral cluster is meant to be the same). It was thus shown for N<sub>2</sub>O [10,11] and CO<sub>2</sub> clusters [12,13] that the broad ‘zero energy resonance’ observed in the early work at energy widths around 0.5 eV [4,7,8], is due to the combined influence of the previously non-resolved, overlapping VFRs and a sharp s-wave type enhancement of the cross section towards zero energy. For XY = N<sub>2</sub>O, the VFRs were found to be extremely sharp with widths between 2 and 5 meV, to exhibit red-shifts of less than one meV per added molecular unit, and to yield predominantly heterogeneous cluster anions (N<sub>2</sub>O)<sub>q-1</sub>O<sup>-</sup> ( $q \geq 5$ ) [10,11], but also homogeneous cluster anions (N<sub>2</sub>O)<sub>q</sub><sup>-</sup> ( $q \geq 4$ ) [11]. For CO<sub>2</sub> clusters [12,13], only homogeneous (CO<sub>2</sub>)<sub>q</sub><sup>-</sup> anions ( $q \geq 4$ ) were observed as decay products of the resonances. Here, the VFRs are significantly broader than those for N<sub>2</sub>O clusters (but still narrow, 10–20 meV) and exhibit larger red-shifts of about 12 meV per added monomer unit [12,13]. These findings show in a direct way that only few neutral precursor cluster sizes  $N$  (mainly one or two) lead to a certain anion size  $q$ . Later studies of the Innsbruck group, carried out at energy widths around 0.1 eV, confirmed these results for N<sub>2</sub>O [15] and CO<sub>2</sub> clusters [16].

A simple model for the electron binding in the VFRs, involving the long-range electron–cluster polarization interaction and an essentially constant short range potential was able to reproduce the size dependent red-shift of the VFRs [11–13] and indicated that the size  $q$  of the observed cluster anions does not differ much from the size  $N$  of the neutral cluster involved in the VFRs which decay to the observed anion (most likely  $q = N$  or  $q = N - 1$ ).

The observation of VFRs requires the existence of weakly-bound diffuse electron states, residing at the surface of the molecule or cluster and corresponding to long-range binding of the electron, e.g. due to dipolar or polarization forces [3,11–13]. They are susceptible to details of the electron–molecule interaction and to the overall strength of the electron–cluster attraction. While VFRs are still present in electron attachment yields for OCS clusters [17] (although less prominent than for CO<sub>2</sub> clusters), they are absent in those for CS<sub>2</sub> clusters [13] (see Refs. [3,17] for a comparative discussion). It is of obvious interest to search for further examples which exhibit VFRs.

In this paper, we report the first high resolution measurements of electron attachment to clusters of sulfur dioxide (SO<sub>2</sub>). As compared to the non-polar linear CO<sub>2</sub> molecule (average polarizability  $2.9 \times 10^{-24}$  cm<sup>3</sup>) [18], a sulfur atom replaces the central carbon atom, leading to a higher molecular polarizability ( $3.8 \times 10^{-24}$  cm<sup>3</sup>) [18]); moreover, SO<sub>2</sub> is bent (angle 119.3° [18]) and possesses a sizeable electric dipole moment (1.633 D [18]). Anion formation (predominantly O<sup>-</sup> production) in electron–SO<sub>2</sub> collisions is mediated by two broad negative ion resonances around 4.6 and 7.2 eV [19–25].

Studies of cluster anion formation resulting from collisions of bound or free electrons with SO<sub>2</sub> clusters started 30 years ago when Bowen and coworkers used energy-variable Rb(5s) atoms as projectiles [26]. The production of (SO<sub>2</sub>)<sub>q</sub><sup>-</sup> anions ( $q = 1–5$ ) was recorded at center-of-mass collision energies from 2 to 6 eV; from

the respective threshold for ion-pair formation, electron affinities of the neutral clusters were estimated.

Subsequently, Märk and coworkers carried out the first study of cluster anion formation in free electron collisions with (SO<sub>2</sub>)<sub>N</sub> clusters over the energy range 0–10 eV at energy widths around 0.5 eV [27,28]. At the energies of the two prominent attachment resonances of the SO<sub>2</sub> monomer homogeneous (SO<sub>2</sub>)<sub>q</sub><sup>-</sup> ( $q = 1–7$ ) anions were found to dominate the mass spectrum with a maximum at  $q = 2$ ; in addition (SO<sub>2</sub>)<sub>q-1</sub>O<sup>-</sup> ( $q = 2–5$ ) and (SO<sub>2</sub>)<sub>q-1</sub>SO<sup>-</sup> ( $q = 2–3$ ) anions were observed (see Fig. 2 in Ref. [28]). At near-zero electron energy, weak signals were detected for the formation of homogeneous (SO<sub>2</sub>)<sub>q</sub><sup>-</sup> anions with  $q \geq 5$  and associated with the action of a ‘zero energy resonance’ in electron attachment to SO<sub>2</sub> clusters [8,28].

Desfrancois et al. [29] investigated electron attachment to SO<sub>2</sub> clusters using laser-excited Xe ( $nf$ ) Rydberg atoms ( $n = 9–35$ ) as a low-energy electron source. Only homogeneous cluster anions (SO<sub>2</sub>)<sub>q</sub><sup>-</sup> ( $q = 1–11$ ) were observed with  $n$ -dependences compatible with an s-wave attachment process. The results were interpreted as electron attachment to a neutral dimer subcluster followed by a rapid impulsive dissociation of the nascent dimer anion with the remaining cluster anions possessing a large amount of internal energy [29].

The photodynamics of small (SO<sub>2</sub>)<sub>q</sub><sup>-</sup> cluster anions has been studied by photodetachment electron spectroscopy [30–34], photodissociation spectroscopy [35,36], and photoelectron-photofragment coincidence spectroscopy [37,38]. This work is complementary to that of anion formation by electron attachment to neutral clusters in the sense that it starts from essentially relaxed anions near the respective ground states.

In the present work, we study SO<sub>2</sub> cluster anion formation by both Rydberg electron transfer (RET) ( $n = 20–260$ ) and free electrons with energies of 0–200 meV at energy widths  $\leq 2$  meV. The results prove the s-wave nature of the primary electron capture process at low energies. At energies just below the excitation thresholds for the three fundamental vibrational modes in the SO<sub>2</sub> molecule [18,39], i.e. bending  $\nu_2$ , symmetric stretch  $\nu_1$ , and asymmetric stretch  $\nu_3$ , peak structure due to VFRs is observed which provides an essential part of the attachment cross section.

## 2. Experimental setup and test measurements

Our experiment is based on the Laser Photoelectron Attachment (LPA) method [3]: state-selected Rydberg atoms or energy-variable, monoenergetic free electrons are created by two-step laser photoexcitation/ionization of potassium atoms via the K(4p<sub>3/2</sub>) level and interact with the target molecules (clusters) of interest in the region where the photoionization process takes place (see Fig. 1 and, for details, previous papers [3,13,17]). For the second step a continuous narrow-band tunable intracavity dye laser (Stilbene 3,  $\lambda_2 = 472–423$  nm, power up to 5 W) is used, thus allowing the excitation of K( $nd, (n-2)s$ ) Rydberg levels with  $n \geq 12$  and the production of free electrons with energies of 0–206 meV at currents of 30 pA. The effective energy width of the free electron collision experiment is influenced by several effects, including photon bandwidth (0.16 meV), residual electric fields, the photoion space charge, and the Doppler effect on the photoelectrons, associated with the motion of the K atoms (mean velocity 600 m s<sup>-1</sup>) and the target species (velocity of SO<sub>2</sub> clusters about 1100 m s<sup>-1</sup>). For the present measurements, the overall energy width was 2 meV or lower, mainly determined by the Doppler broadening, amounting to  $\Delta E_D \approx 0.1E^{1/2}$  meV (electron energy  $E$  in meV), and the space charge broadening of about 1 meV at the current 30 pA [3].

The target beam has a diameter of 3 mm in the reaction region and originates from a nozzle with 60  $\mu$ m diameter at a nozzle

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