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IP determination and 1+1 REMPI spectrum of SiO at 210–220 nm in an ion trap: Implications for SiO⁺ ion trap loading



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ABSTRACT

The 1+1 REMPI spectrum of SiO in the 210–220 nm range was recorded. Observed bands were mostly assigned to the vibrational bands $v'' = 0 - 3$, $v' = 5 - 10$ of the $A - X$ electronic transition. Additionally, a band near 216–217 nm was tentatively assigned as a 2-photon transition from X to the $n = 12, 13$ [$X^2\Sigma^+$, $v^+ = 1$] Rydberg states. Based on observed lines we estimated the IP of SiO to be 11.594(5) eV. The SiO⁺ cation has previously been identified as having a cycling transition useful for state control by optical pumping. Our work allowed us to identify an efficient method for loading an ion trap with rotationally and vibrationally cold SiO⁺ from an ablated sample of SiO by photoionizing through the ($5,0$) $A - X$ band at 213.977 nm.

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1. Introduction

Interest in spectroscopy of SiO and SiO⁺ was initially stimulated by astrochemistry. After detection of vibrational bands of SiO in stellar atmospheres [1] a search for electronic transitions followed. Several studies investigated transitions of SiO in the UV region [2,3]. The ionization potential (IP) of SiO was measured by means of electron impact [4], spectroscopy of Rydberg states [5], photoelectron spectroscopy (PES) [6], and direct VUV photoionization [7]. SiO⁺ bands were observed in 1943 [8] but at that time misidentified as SiN. Later, this misunderstanding was resolved [9] and several electronic states were mapped by means of PES [6], absorption spectroscopy [9,10] and laser-induced fluorescence (LIF) [11]. Several computational studies [12–14] predicted rich excited electronic state structure of SiO⁺. Ion chemistry of the Si⁺/O₂ system and physics of ablation of SiO was studied in several works [15–17], stimulated by interest in Si clusters and vapor deposition.

Our interest in SiO and SiO⁺ is primarily motivated by its properties that make it amenable to laser control of internal and external degrees of freedom [18,19]. Control of molecules offers new applications in precision measurements of fundamental constants and ultracold chemistry [20–22]. The quantum state preparation necessary for coherent control is a serious technical challenge for molecules as rotational and vibrational degrees of freedom significantly complicate the internal structure compared to atoms. The $B^2\Sigma^+ - X^2\Sigma^+$ electronic transition of SiO⁺ has highly diagonal Franck-Condon factors [18,23] and well-separated P and R

branches, which make it suitable for broadband rotational cooling [24,25]. To design a laser cooling scheme for SiO⁺, accurate knowledge of branching fractions of SiO⁺ radiative relaxation to low lying vibrational and electronic states is necessary. The previous measurement of the branching fractions of $B^2\Sigma^+$, $v = 0$ emission to excited vibrational levels of $X^2\Sigma^+$ found branching to the $X^2\Sigma^+$, $v = 1$ state to be 3% relative to the $X^2\Sigma^+$, $v = 0$ state, while branching to higher vibrational levels and the low-lying $A^2\Pi$ state could not be detected [23]. Refining the limits on branching to higher lying states is necessary before the efficacy of a laser cooling scheme can be predicted.

To enhance the sensitivity of SiO⁺ spectroscopy measurements, a system was designed that can trap large numbers of SiO⁺ ions in a linear Paul trap and perform dispersed LIF measurements to extract branching fractions. The work in this paper was motivated by the need for a reliable, rapid, and pure source of SiO⁺. Efficient and reliable loading of SiO⁺ into a Paul trap can be achieved by means of photoionization. SiO has a relatively high ionization potential (> 11 eV), therefore a multiphoton process is needed to photoionize it with commonly available laser light sources. The simplest and most convenient multiphoton ionization scheme would be two photon one color photoionization enhanced by resonance absorption of the first photon or 1+1 resonance-enhanced multiphoton ionization (1+1 REMPI). The $A^1\Pi - X^1\Sigma^+$ band system enables 1+1 REMPI for photoionization of SiO. The system has previously been studied via LIF [26] and absorption measurements [27]. The origin of this band is located at 5.3 eV, slightly below half the ionization energy of SiO; its vibrational overtones with $\Delta v \geq 5$

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are energetically allowed for 2-photon 1-color photoionization. Photoionization via this band system has the additional advantage for trap loading that one can select ionization pathways to produce SiO^+ only slightly above the ionization threshold, i.e. in the ground vibrational and electronic state and with low rotational energy.

No previous 1+1 REMPI photoionization study of this system exists. The ionization energy of SiO has not been measured with precise methods such as PFI ZEKE. The most precise values measured by photoelectron spectroscopy [6] and synchrotron-based absorption spectroscopy of Rydberg series [5] are only accurate within $\sim 80\text{--}100\text{ cm}^{-1}$ and contradict each other. The photoionization spectrum shape near the ionization threshold can be modified by highly excited states of a neutral molecule, e.g. Rydberg states. Therefore, the spectrum band intensities are not straightforward to predict based on thermal populations in the lower state and vibrational overlap between the neutral and the cation wavefunctions. Instead, direct measurements of photoionization spectra can be used to locate intense and state-selective bands for SiO^+ loading. This work reports the 1+1 REMPI spectrum of SiO in the 210–220 nm range. The spectrum consists mostly of energetically allowed 1+1 REMPI bands via the $A-X$ transition. It also reveals several new features due to highly excited Rydberg states of SiO and results in accurate determination of the IP of SiO .

2. Experimental

All REMPI measurements occurred under UHV (5×10^{-10} Torr) conditions with the aid of a home built linear Paul trap for ion storage and a channel electron multiplier (CEM) for ion detection. A pressed pellet of SiO , situated below the center of the Paul trap, was ablated by 532 nm light produced by frequency doubling of a pulsed Nd:YAG laser. Photoionization was subsequently performed on the ablation plume inside the trapping volume. After accumulating ions from a predetermined number of photoionization and ablation pulses, the trapped ions were released and detected by the CEM.

The experimental setup is shown in Fig. 1. The vacuum chamber housed the Paul trap (3.6 MHz trap frequency, $r_0 = 3$ mm, $z_0 = 7.29$ mm, $V_{pp} = 660$ V, $\kappa = 0.22$, $V_{ec} \approx 1$ V), an ablation target of pressed SiO located 1 cm below trap center, and the CEM. The CEM was kept at -3 kV throughout the duration of the experiment. The 532 nm ablation laser light was generated by frequency doubling of an Nd:YAG laser output (Continuum Minilite II, 10 Hz rep rate, 3–5 ns pulse width), attenuated by a $\lambda/2$ waveplate and a polarizing beam splitter to ~ 0.5 mJ. The 532 nm light passed through a motor-controlled rotating window, and was focused onto the sample with an $f = 150$ mm lens. The rotating window was positioned at a $\sim 30^\circ$ angle with respect to the ablation beam axis to parallel shift it. As the window rotated, the beam was walked in a circle to refresh the ablated surface.

The laser light used for photoionization was generated by an Nd:YAG pumped OPO system (Ekspla NT342/1/UVE OPO, 10 Hz rep rate, 4.2 ns pulse width, 4 cm^{-1} linewidth) and focused into the trapping volume with an $f = 200$ mm lens. The photoionization laser pulse was delayed by 90 μs with respect to the ablation laser. The REMPI signal was found to stay constant over a delay range of $\sim 50\ \mu\text{s}$. The average pulse energy of the photoionization laser was typically 0.5 mJ. A photodiode located after the vacuum chamber along the beam path was used to monitor the output power.

The wavelength of the photoionization laser was scanned from 210 to 220 nm in steps of 0.025 nm. At each wavelength, the ablation laser and REMPI laser pulsed 5–20 times. After that the RF trapping voltage was linearly ramped down over 0.5 ms and the accumulated ion products were detected by the CEM. Event counting was used to quantify the ion signal. The number of events

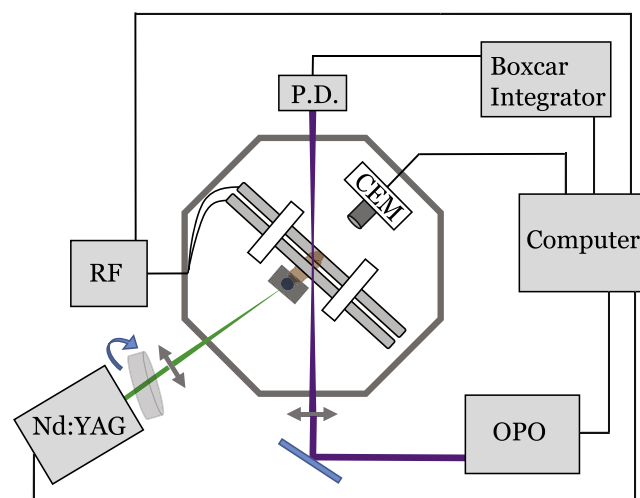


Fig. 1. Schematic diagram of the experimental setup.

detected per 0.5 ms voltage ramp did not exceed several thousand with typical values around several hundred. Care was taken to avoid saturation effects due to filling the ion trap. A boxcar integrator was used to record the average voltage of the photodiode measuring the REMPI laser output to provide (linear) power normalization of the REMPI signal under the assumption that the $A-X$ transition was saturated and the second, photoionizing one was not. This detection sequence was repeated several times to accumulate statistics before the wavelength was changed. After completion of a wavelength scan over a given range its direction was reversed to discriminate against drifting of the REMPI signal.

3. Calculations

All electronic structure calculations were performed with the QChem package. The IP of SiO was calculated at CCSD(T)/CBS level. The potential energy curves of the ground electronic states of SiO and SiO^+ were calculated at IP-EOM-CCSD level and fitted to a Morse potential to determine R_e . The values obtained for the neutral SiO ($R_e = 1.5094$ Å) and for SiO^+ ($R_e = 1.5166$ Å) are in very good agreement with experimentally measured values [28,29]. CBS extrapolation was achieved by fitting CCSD(T)/aug-cc-pVnZ ($n = 2\text{--}5$) ground electronic state energies of SiO and SiO^+ with the mixed exponential/Gaussian formula [30]. The adiabatic IP value was obtained by subtracting the CCSD(T)/CBS energy of SiO from that of SiO^+ and correcting for the zero-point energies. The resulting value was IP = 11.6138(1) eV where the number in parenthesis is the $1\text{-}\sigma$ of the exponential fit parameter.

4. Notation

The following notation is used throughout the paper. Rotational and vibrational levels of the ion are followed by the superscript “+” sign, such as N^+ or v^+ . Quantum numbers of the ground state of SiO , $X^1\Sigma^+$ are followed by double prime, e.g. J'' and v'' . Energy levels of $A^1\Pi$ state of SiO are followed with a single prime, e.g. J' and v' . We use the total rotational quantum number J for the neutral SiO and the nuclear rotational quantum number N^+ for SiO^+ to avoid dealing with half-integer J^+ values. Rydberg states of SiO are denoted with the Rydberg electron configuration in parenthesis, e.g. $(ns\sigma)$, which is followed by the state term symbol, e.g. $^1\Sigma^+$ and the level of the SiO^+ ion core, e.g. $[X^2\Sigma^+, v^+ = 1]$, in square brackets.

5. Results

Fig. 2 presents the 1+1 REMPI spectrum of neutral SiO at 210–220 nm. The upper black trace is experimental data; the colored lines below are simulated transitions. The spectrum consists of two types of features. The first type is the red-degraded bands distributed over the 210–218 nm range. The second type is a complex band at 216 nm with multiple narrow lines. After 218 nm the signal is small and unresolved. The rotational lines of SiO could not be resolved since the bandwidth of the photoionization laser is 4 cm^{-1} , and the rotational constant of SiO is 0.72 cm^{-1} . Therefore the observed bands represent rotational contours of vibronic transitions of SiO.

The bands of the first type were assigned as ($v' = 5 - 10, v'' = 0 - 3$) vibrational bands of the $A - X$ electronic transition (see Table 1 and Fig. 2); they are red-degraded since the rotational constant of the A state is smaller than that of the X state (0.62 cm^{-1} vs 0.72 cm^{-1} for B_0). The intensity of the bands was well reproduced by the Franck-Condon coefficients of SiO $A - X$ transition [31] multiplied by a sum of the FCFs of the energetically allowed $X^+ - A$ ionization channels. The best agreement was achieved when both rotational and vibrational temperatures were equal to 1000 K, which is reasonable given the high temperatures of ablation plumes. The 5–0 rotational band contour at 214 nm looks different from other $A - X$ bands and the intensity of this band is not reproduced by Franck-Condon simulations. The reason for this difference is that the 2-photon excitation on the 5–0 transition brings SiO very close to the ionization threshold level where angular momentum conservation restricts ionization for high rotational levels (see discussion below).

The second type of band, observed at 216–217 nm, is qualitatively different from the $A - X$ bands. Instead of a red-degraded contour it has several sharp peaks that resemble Q-branches of electronic transitions between states with similar values of rotational constants. Since there are no electronic states with $B' \approx B''$ in the one-photon energy range, states responsible for the observed band are likely excited in 2-photon excitations. We tentatively assign this band to a two-photon transition from the $v'' = 1, X^1\Sigma^+$ state of SiO to the Rydberg states with $n = 12, 13$ converging to the $v^+ = 1, X^2\Sigma^+$ ion core. The assignment is based on energetics and on the “vertical” appearance of the observed bands which results from $B^+ \approx B'$. Since the SiO and SiO⁺ ground electronic states have similar bond lengths and vibration frequencies, the $v'' = 1 - v^+ = 1$ excitations have a favorable Franck-Condon overlap. The 2-photon excitation at 216 nm is enhanced by the first

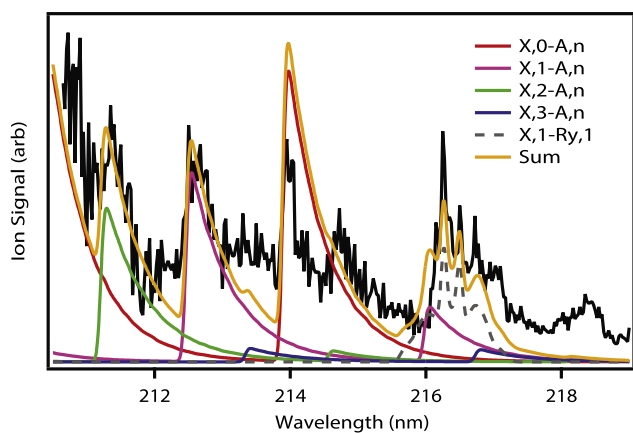


Fig. 2. SiO 1+1 REMPI spectrum as a function of UV wavelength at 210–220 nm. The black trace is experimental data and colored traces are simulated transitions (see legend).

Table 1

Assignment of 1+1 REMPI spectrum of SiO. The energy of SiO above the ionization threshold after 2-photon absorption, ΔE , is calculated assuming IE = 11.586 eV.

| λ (nm) | $(v' - v'')$ Assignment | $\Delta E(\text{cm}^{-1})$ |
|---------------------|------------------------------------|----------------------------|
| 210.47 ^a | (6–0), $A - X$ | 1579 |
| 211.29 ^a | (9–2), $A - X$ | 3671 |
| 212.54 ^a | (7–1), $A - X$ | 1882 |
| 213.43 ^a | (10–3), $A - X$ | 3951 |
| 213.98 ^a | (5–0), $A - X$ | 23 |
| 214.66 ^a | (8–2), $A - X$ | 2185 |
| 216.06 ^a | (6–1), $A - X$ | 349 |
| 216.26 ^b | $(s\sigma)^1\Sigma^+ - X, v'' = 1$ | ~240 |
| 216.49 ^b | $(p\sigma)^1\Sigma^+ - X, v'' = 1$ | ~140 |
| 216.58 ^b | $(d\sigma)^1\Sigma^+ - X, v'' = 1$ | ~100 |
| 216.81 ^a | (9–3), $A - X$ | 2489 |
| 218.19 ^a | (7–2), $A - X$ | 676 |

^a 1+1 REMPI via the $A - X$ system.

^b Tentative assignment of 2-photon excitation of Rydberg states $n = 12, 13$ with an ion core of $[X^2\Sigma^+, v^+ = 1]$.

photon being in near resonance with the 6–1 vibrational band of the $A - X$ system.

The 2-photon selection rules allow excitation of Rydberg states of Σ, Π and Δ symmetry. In the simulation we used the 3 Rydberg states of Σ^+ symmetry to simulate the band shape and achieved good agreement with experimental results; however, this assignment is tentative and higher precision data is needed to assign the electronic symmetry of the states involved in this second type of band.

The list of observed transitions is shown in Table 1 along with vibrational assignments and the energy difference, ΔE , between the ionization energy of SiO and the energy of SiO after 2-photon absorption.

We recorded the Ba photoionization spectrum to quantify the ionization potential depression due to the electric field of the trap (Fig. 3). The onset of the Ba⁺ ion signal is observed at 41936 cm^{-1} , which is 99 cm^{-1} below the ionization energy of Ba. The weak Ba⁺ signal observed below the onset is due to ionization of metastable excited states of Ba populated during ablation, probably belonging to the ³D term. The difference between the observed and the actual ionization threshold is due to ionization of Rydberg states lying

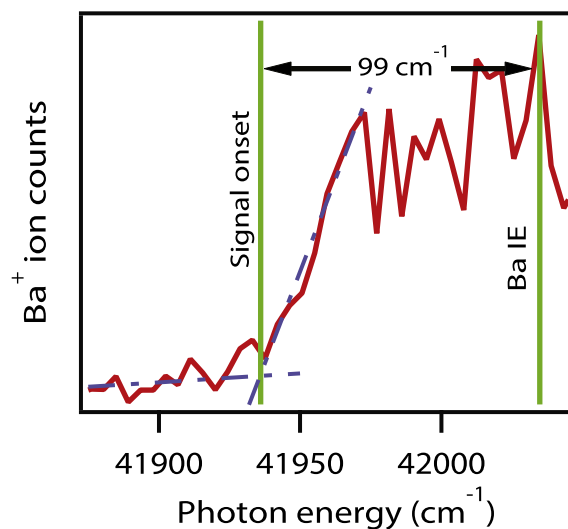


Fig. 3. 1-photon photoionization spectrum of Ba in the ion trap (red trace). Dashed blue lines extrapolate the signal rise and the background to find the onset. Observed onset of ionization and field-free ionization energy of Ba are marked with vertical green lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

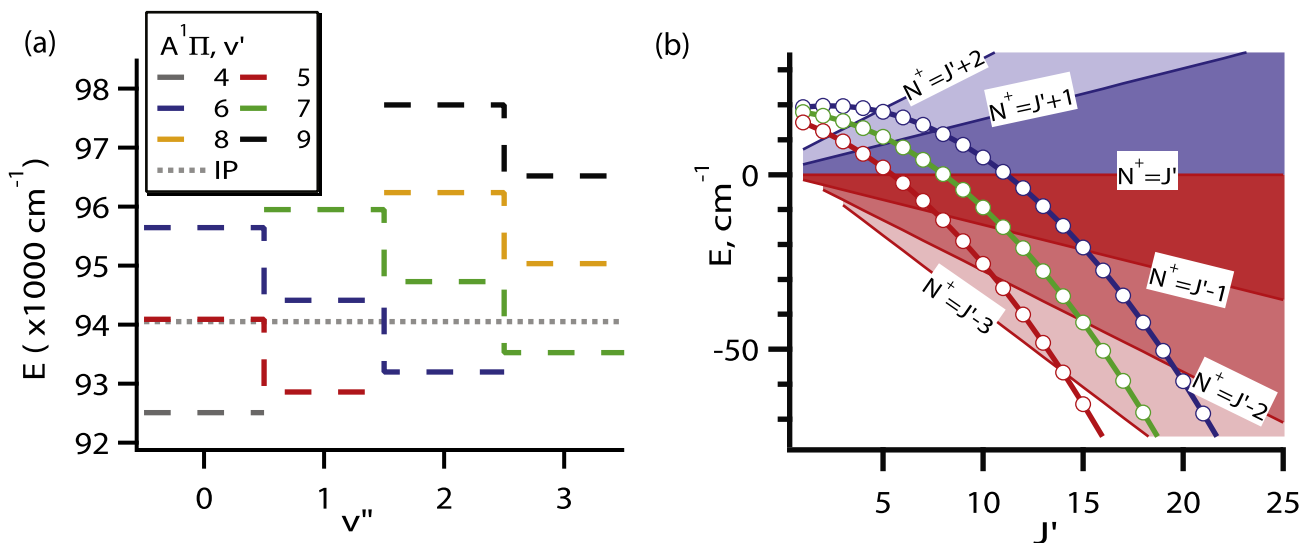


Fig. 4. (a) The energy of SiO after a 2-photon transition via vibrational bands of A – X transitions; (b) The energies of rotational levels of SiO after a 2-photon excitation of the (5,0) A – X transition.

below the ionization threshold by the electric field of the trap (see discussion).

6. Discussion

The photon energy required for photoionization of SiO in a 1-color 2-photon transition can be defined as

$$h\nu \geq \frac{IE_{\text{SiO}} - E_i - \Delta E_F}{2} \quad (1)$$

where IE_{SiO} is the field-free ionization energy of SiO, E_i is the energy of the initial state of SiO, and ΔE_F is the depression of IE_{SiO} due to the electric field in the trap. Assuming that SiO is produced by ablation in the ground electronic state or quickly quenched to it by means of radiation and collisions, E_i is due to the vibrational and rotational population of the ground state. Fig. 4a shows the energies of SiO after resonant 2-photon excitation on the A – X transition with $v'' = 0 - 3$ relative to IE_{SiO} . The energies in this diagram are relative to the minimum of the $X^1\Sigma$ potential energy curve. The dashed grey line is the ionization energy of SiO in our trap for which we used the $IE_{\text{SiO}} - \Delta E_F$ value of 11.586 eV estimated from our data (see below). To ionize SiO in the trap, two photons must promote it above this level. For example, SiO molecules at $v'' = 0$ can be ionized via A – X when $v' \geq 5$, ionization of $v'' = 1$ requires $v' \geq 6$ etc. Higher v'' levels require correspondingly higher v' levels of the A state of SiO. Bands with $\Delta v \leq 4$ cannot be observed in 1+1 REMPI spectrum, while all bands with $\Delta v = 5$ are located above the IE_{SiO} level. The 5 – 0 band is only $\sim 23 \text{ cm}^{-1}$ above the estimated value of IE_{SiO} . The rotational structure of this band is affected by proximity of the IE_{SiO} .

Fig. 5 expands part of the SiO REMPI spectrum at 214 nm where the 5 – 0 band is located. It has an abrupt drop of ion signal near 214.05 nm. The SiO A – X spectrum simulation suggests that the drop occurs near the P(11), Q(15) and R(20) rotational lines. Fig. 4b shows the energy levels of SiO excited with 2-photon absorption via rotational levels of the 5 – 0 band. The red¹, green and blue curves with hollow circles denote excitation via P, Q and R rotational branches respectively. The energy scale is relative to

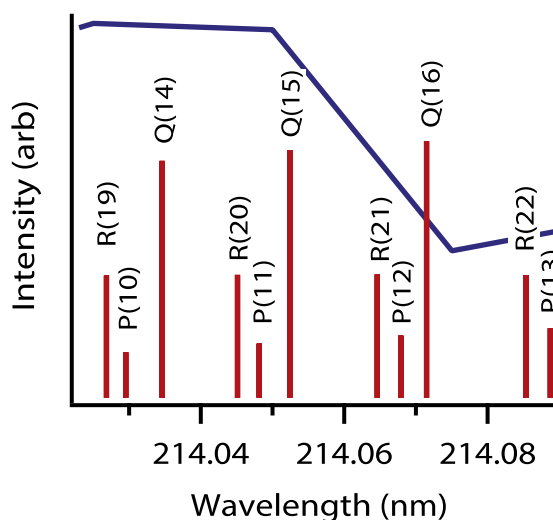


Fig. 5. The 5 – 0 band of A – X of SiO near 214.05 nm (blue dotted line) overlaid with simulated rotational line positions (red vertical lines). The observed beginning of the cut-off corresponds to Q(15), P(11) and R(20) rotational lines which is consistent with the prediction made above using Fig. 4b with IP = 11.586 eV. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the energy of the rotational levels of SiO⁺, i.e. the horizontal line at $E = 0 \text{ cm}^{-1}$ corresponds to the SiO⁺ molecules with $N^+ = J'$, the slanted straight lines below the horizontal line correspond to $N^+ = J' - 1, J' - 2$, and $J' - 3$, while those above it correspond to $N^+ = J' + 1$ and $J' + 2$. The Q line crosses $N^+ = J'$ line near Q(8), $N^+ = J' - 1$ line near Q(11) and $N^+ = J' - 2$ line near Q(15). The crossings define the levels at which 2-photon ionization cannot produce SiO⁺ molecules with N^+ equal or higher than the corresponding J' .

The abrupt drop of signal in the 5 – 0 band is consistent with reduced photoionization efficiency for excitation that must occur via lines with $N^+ < J' - 2$ as shown in Fig. 4b. While ionization via these lines is energetically allowed if SiO⁺ is produced at lower N^+ levels, angular momentum conservation requires the electron to detach as a high angular momentum partial wave. For example, ionization via the Q(16) line can produce SiO⁺ with $N^+ < 13$. If the

¹ For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

photoionization of SiO obeys the Hund's case (b) selection rule [32], a transition with $|\Delta N| \leq l + 1$ for $N^+ = 13$ requires $l \geq 2$.

It was shown in [33] that the cross sections for photoionization of neutral particles tends to non-zero values near the threshold even for high angular momentum waves of the electron. In other words, partial waves of the electron near threshold are not limited to $l = 0$ or 1, higher l partial waves occur. Since total angular momentum is conserved, high values of l allow large $\Delta J = J'' - J^+$ change during photoionization. On the other hand, several studies with PFI-ZEKE technique explored rotationally resolved spectra of different molecules near threshold. It was found that there are no strict selection rules but in many cases "propensities" for a small change of angular momentum upon ionization exist [34,35], where lines with $\Delta J \leq 5/2$ are largest and intensity quickly falls off for higher ΔJ .

The abrupt drop of signal in the 5–0 band near Q(15) line is consistent with $l = 0$ or 1, i.e. propensity for small ΔJ change upon photoionization. If large ΔJ were allowed, one would expect a gradual reduction of intensity in the 5–0 band as progressively larger ΔJ values are reached at higher rotational lines (e.g. $\Delta J = 5/2$ at Q(15), $\Delta J = 7/2$ at Q(19) etc). Limiting l to 0 and 1 results in $|\Delta J| \leq 5/2$ or $|\Delta N| \leq 2$ propensity. The value of $IE_{SiO} - \Delta E_F$ of 11.586 eV satisfies this propensity simultaneously for R(18), Q(15) and P(11) lines of the 5–0 band (see Fig. 4b), in good agreement with the rotational levels near the cut-off in Fig. 5. It is possible to satisfy the requirement of $|\Delta J| \leq 3/2$ or $|\Delta N| \leq 1$ for R(18), Q(15), and P(13) lines with a value of 11.583 eV, however it is in worse agreement with the observed cut-off. Propensities for $|\Delta J|$ values higher than 5/2 are in even worse agreement with the observations. Therefore, we picked the value of 11.586 ± 0.003 eV for $IE_{SiO} - \Delta E_F$ of SiO, where the uncertainty of 3 meV is due to a possibility of $\Delta J = 1$ error in the propensity for rotational levels change.

To obtain IE_{SiO} we have to account for depression of the ionization energy by the electric field in the quadrupole trap. The value of the IP depression, ΔE_F , is proportional to the square root of the electric field and may be estimated by the formula

$$\Delta E_F = c\sqrt{F} \quad (2)$$

where F is the field in units of V/cm, ΔE_F is in cm^{-1} , and $c = 4 - 6$ depending on the mechanism of ionization [36]. For diabatic ionization of Rydberg states $c = 4$ and for adiabatic ionization $c = 6$. The choice of mechanism depends on the slew rate of the electric field. When the slew rate is high, components of Stark manifolds diverge in energy without mixing and the diabatic mechanism is preferred. For a low slew rate or DC field the Stark states have enough time to mix and the ionization is adiabatic. We expect that the trap RF field acting on Rydberg states for many periods will mix the Stark states and result in adiabatic ionization.

The depression of 99 cm^{-1} corresponds to a field of 270 V/cm for Ba ions. The difference in molecular mass of Ba and SiO affects their relative stability in the trap, i.e. SiO^+ formed in a field of 270 V/cm may not be trapped as efficiently as Ba^+ . We performed an ion trajectory simulation with SIMION 8.0 [37] where 1000 ions of $m/z = 138$ and 44 were randomly generated inside the ion trap along the photoionization laser beam and their trajectories were simulated for 10 μs . Our simulations show that 61% of all trapped Ba^+ ions were created in a field ≤ 270 V/cm. In the SiO simulation the same fraction (61%) of the trapped ions were created in a field ≤ 130 V/cm. Depression of IE_{SiO} by such a field is $6 \times \sqrt{130(\text{V}/\text{cm})} = 68 \text{ cm}^{-1}$ or ~ 8 meV. We estimate that the uncertainty of that figure is not more than 4 meV which equals the difference with the measured ΔE_F for Ba. Including these considerations yields an estimate of IE_{SiO} of 11.594 ± 0.005 eV. This value is within error bounds of the most reliable previous mea-

surements [4–7]. Interestingly, the current measurement is almost halfway between the most accurate values obtained with PES [6] (11.61(1) eV) and a Rydberg formula fit [5] (11.584(11) eV) and is within the error bounds of both of them.

Our theoretical prediction for the IP = 11.6138(1) eV overestimates the experimental value by ~ 20 meV. It is in good agreement for the CCSD(T)/CBS method which is known to achieve an accuracy of 10–20 meV in IP calculations [38]. The discrepancy between measured and calculated values may be due to unaccounted effects, such as relativistic motion or core correlation, and from high level dynamic correlation missing in CCSD(T). Previous calculations by Das et al. [13] underestimated the IP by ~ 0.7 eV, probably because the MRDCI method could not treat the dynamic correlation in SiO^+ and SiO at the same level.

The sharp bands near 216 nm were assigned to 2-photon Rydberg states transitions. To be prominent in the 1+1 REMPI spectrum, the 2-photon Rydberg state transition must have: (1) good FC overlap with the lower state, (2) high electronic transition probability, e.g. low principal quantum number and resonance enhancement for the 1-photon absorption, (3) high Boltzman population of the lower state, and (4) should be above the ion ground state to autoionize. Based on these assumptions, the Rydberg states involved in this transition is likely due to $(n\sigma, np\sigma, nd\sigma) \ ^1\Sigma^+$ [$X^2\Sigma^+, v^+ = 1$] and $(nd\delta) \ ^1\Delta$ [$X^2\Sigma^+, v^+ = 1$] Rydberg states with $n = 12, 13$. These states are located ~ 900 – 1100 cm^{-1} below the $v^+ = 1$ level and above the IP of SiO. The lower state $X, v'' = 1$ has significant population at a temperature of 1000 K and the transition is resonantly enhanced due to the proximity to the $A, v' = 6$ level. Frank-Condon overlap favors transition from $v'' = 1$ to $v^+ = 1$ since SiO and SiO^+ have sufficiently similar bond length and vibrational frequency.

Using 1+1 REMPI on stronger bands of the $A - X$ transition resulted in several thousand SiO^+ ions loaded per single ablation event followed by REMPI ionization. The most convenient loading transition is (5,0) of $A - X$ at 213.977 nm as it is intense and SiO^+ can be loaded with only ~ 30 – 300 cm^{-1} of internal energy. Therefore, loading of vibrationally or electronically excited SiO^+ is avoided and the rotational temperature of loaded ions is significantly lower than that of the ablated SiO. Another advantage of the (5,0) transition is that it is not resonant with the $A - X$ and $B - X$ bands of the NO molecule, lying near 215 nm [39]. NO has a relatively low IP of ~ 9.26 eV [40] and can be 2-photon ionized below 267 nm. Even though ultrahigh vacuum is used in this work and the NO_x ($\text{NO} + \text{NO}_2$) concentration in the air is < 1 ppm, there is enough NO in the vacuum chamber to load a few NO^+ cations per laser pulse with 1+1 REMPI.

Depending on the RF amplitude used for the ion trap, depression of IE_{SiO} by the electric field may not be sufficient to ionize SiO via the (5,0) transition. In this case, an alternative is to use the transitions near 216–216.5 nm range which originate at $v'' = 1$ and produce SiO^+ up to 100–350 cm^{-1} above its ground state origin.

7. Conclusions

The 1+1 REMPI spectrum of SiO in the 210–220 nm range was recorded. Observed bands were assigned to the $A - X$ band system and 2-photon transitions were tentatively assigned to the $n = 12, 13 (n\sigma, np\sigma, nd\sigma) \ ^1\Sigma^+$ and $(nd\delta) \ ^1\Delta$ [$X^2\Sigma^+, v^+ = 1$] Rydberg states. The characterized photoionization channels allow for loading SiO^+ ions into an ion trap where proper selection of the ionization channel allows for loading vibrationally and rotationally cold SiO^+ . The observed spectrum enabled a more accurate estimation of the SiO IP than previous measurements with a value of 11.594 (5) eV.

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