

Calculated two-photon electronic transitions in sulfuric acid and its atmospheric relevance

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ABSTRACT

We have calculated two-photon electronic transitions for sulfuric acid (H_2SO_4) in the ultraviolet region using coupled cluster quadratic response theories combined with correlation consistent basis sets. We have investigated how the intensity of two-photon electronic transitions in H_2SO_4 depends on the wavelength of the photons absorbed. We find that the intensity is more or less constant in the wavelength region in which the density of solar flux is of any importance. We have calculated the J -values for the photodissociation of H_2SO_4 with absorption of two photons and compared these with previously calculated J -values for one-photon absorption. We find that two-photon electronic transitions of H_2SO_4 are not a significant mechanism in the photodissociation of H_2SO_4 .

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1. Introduction

As the focus on global climate change has increased, so has the research of sulfur containing compounds. The anthropogenic emission of sulfur has increased significantly during the last 150 years [1] and surpassed the natural emission in the 1950s. In periods of little volcanic activity, the oceans are the largest natural source of atmospheric sulfur emissions. Sulfur is here emitted in a reduced form, predominantly as dimethyl sulfide (DMS) [2]. DMS is oxidized to OCS, which diffuses through the troposphere into the stratosphere where further oxidation to sulfur dioxide (SO_2), sulfur trioxide (SO_3) and eventually H_2SO_4 occur [1–4].

In the stratosphere and mesosphere, H_2SO_4 is the dominant form of sulfur [5]. H_2SO_4 is very hygroscopic and readily forms hydrated aerosols in the lower stratosphere, where these take part in the global stratospheric aerosol layer. However, above 35 km the concentration of water is lower and H_2SO_4 is primarily found in a gaseous form [6]. Investigations of the geochemical sulfur cycle are very important in order to understand the effects on local and regional environments (tropospheric sulfur), but also on climate and chemistry (stratospheric sulfur).

In the stratosphere, H_2SO_4 is photolysed to SO_3 , which is subsequently photolysed to SO_2 . The photodissociation process of H_2SO_4 was initially thought to occur via electronic excitation in the UV region [6,7]. However, both experiments and *ab initio* calculations

have repudiated this [8–12]. Attempts to measure the absorption spectrum of H_2SO_4 up to 140 nm (8.6 eV) have failed to identify any electronic transitions [5,8]. The most recent calculations, show that the lowest lying electronic transition in H_2SO_4 occurs at ~ 139 nm, resulting in an estimated cross section in the actinic region that is significantly lower than the measured upper limits [10–12]. Hence, photolysis via electronic transitions are unlikely in the stratosphere.

Calculations suggest that excitation of OH-stretching overtones in H_2SO_4 with near-infrared and visible photons can provide sufficient energy for the photodissociation [12–15]. The energy required for dissociation of H_2SO_4 has been calculated [14–16] with the most accurate value of $36.0 \text{ kcal mol}^{-1}$ obtained with use of the CCSD (T)/aug-cc-pV(T + d)Z method [16]. An OH-stretching transition with $\Delta v \geq 4$ (39 kcal mol^{-1}) should therefore provide sufficient energy for dissociation [14]. The timescale and quantum yields of the dissociation reaction have been calculated and found to be reasonable for the reaction to occur in the atmosphere [17]. Later, it was also suggested that the dissociation at high altitude could occur via vacuum UV electronic transitions in the Lyman- α region (121.6 nm, 10.2 eV) [18]. Even though the Lyman- α solar flux has a narrow band, the cross section of H_2SO_4 is very large in this wavelength region [11,12].

The photodissociation mechanism of H_2SO_4 is altitude dependent [11,12,14]. While the solar flux in the visible region is more or less constant at all altitudes, this is not the case in the Lyman- α region, with the solar flux being much larger at high altitudes. The dominant photodissociation mechanism of H_2SO_4 below 70 km was concluded to be absorption in the visible region by

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OH-stretching overtone transitions, and above 70 km absorption of radiation in the Lyman- α region involving excited states with large Rydberg character [11,12,14].

An interesting alternative is to consider two-photon excitation to the lower lying electronic states as a competing photodissociation mechanism of H_2SO_4 in the atmosphere. Two-photon excitation to the lowest lying electronic states in H_2SO_4 could be achieved with photons with wavelength of ~ 280 nm; photons that are much more abundant in the atmosphere, than the ~ 140 nm photon required for one-photon electronic excitation. We have calculated two-photon excitation energies and intensities for the 8 lowest lying electronic states in H_2SO_4 . Furthermore, we suggest a way to calculate the J -value for dissociation of a molecule by two-photon electronic transitions, and we calculate the J -value for photodissociation of H_2SO_4 via two-photon absorption, at altitudes of 30 and 100 km. We compare our calculated two-photon J -values with previously calculated one-photon J -values. Previously, the atmospheric production of OH radicals by a sequential two-photon excitation mechanism has been suggested to be of potential interest [19].

2. Theory and calculations

Vertical excitation energies were calculated by linear response theory and are the same for one and two photon excitations. Intensities of the two-photon excitations were calculated by quadratic response theory. Both excitation energies and intensities were calculated with the DALTON program [20]. We have used a hierarchy of coupled cluster response methods, including the coupled cluster singles (CCS), the second order approximated coupled cluster singles and doubles (CC2), and the coupled cluster singles and doubles (CCSD) methods. Coupled cluster response theory has previously been shown to give highly accurate results for both one-photon electronic excitation [21–23] and calculations of non-linear response functions [24,23], from which the two-photon excitation is derived. We have used the Dunning type correlation consistent basis sets supplemented with additional tight d basis functions on sulfur; cc-pV(D+d)Z, aug-cc-pV(D+d)Z, and cc-pV(T+d)Z [25–27]. We refer to these as V(D+d)Z, AV(D+d)Z, and V(T+d)Z, respectively. The additional tight d functions have been shown to significantly improve the geometries and energies of sulfur containing compounds [28,29]. We investigate how the intensity of a two-photon electronic transition in H_2SO_4 depends on the frequency of the photons absorbed, using the less computationally demanding, density-functional response theory hybrid Becke-3-parameter-Lee-Yang-Parr (B3LYP) functional [30–32]. All the electrons were correlated in the computations. Calculations were performed on the experimental geometry of H_2SO_4 [33].

The transition moments for an absorption of two photons with identical frequency can be given as the sum-over-states expression [34,35]

$$M_{f-g}^{\alpha\beta}(\omega) = \sum_i \frac{\langle \Psi_g | \mu_\alpha | \Psi_i \rangle \langle \Psi_i | \mu_\beta | \Psi_f \rangle}{\omega_i - \omega} + \frac{\langle \Psi_g | \mu_\beta | \Psi_i \rangle \langle \Psi_i | \mu_\alpha | \Psi_f \rangle}{\omega_i - \omega} \quad (1)$$

$$M_{f-g}^{\alpha\beta}(\omega)^* = M_{g-f}^{\alpha\beta}(-\omega) \quad (2)$$

where Ψ_g , Ψ_i , and Ψ_f are the wave function for the ground, intermediate, and final electronic states, ω_i is the transition energy from ground state to the intermediate state, ω is the energy that corresponds to the specific frequency of the photons used to probe the molecule, and μ_α and μ_β are the α and β components, respectively, of the dipole moment operators ($\alpha, \beta = x, y, z$). In exact response theory the two-photon transition moments are symmetric with respect to complex conjugation and sign inversion of the frequencies, resulting in transition moments that are real. However, in coupled cluster response theory there exists no such complex conjugations, since a

biorthonormal parameterization is used [36]. Instead one works with two-photon transition strengths, which are obtained as a symmetrized product of ‘left’ and ‘right’ transition moments [37]

$$S_{\alpha\beta,\gamma\delta}^{\text{gf}} = \frac{1}{2} (M_{g-f}^{\alpha\beta}(-\omega) M_{f-g}^{\gamma\delta}(\omega) + M_{g-f}^{\gamma\delta}(-\omega) M_{f-g}^{\alpha\beta}(\omega)^*) \quad (3)$$

When the two-photon transition strength for photons of any polarization is averaged over all orientations of the absorbing molecule, the result is [38]

$$\delta^{\text{TP}} = F\delta_F + G\delta_G + H\delta_H \quad (4)$$

where δ_F , δ_G , and δ_H are molecular parameters, and F, G, H are coefficients depending on the polarization of the incident laser beams. For our calculations we only use linear parallel polarized light, and the coefficients are then $F = G = H = 2$ [36]. The three parameters δ_F , δ_G , and δ_H will be calculated as [36]

$$\delta_F = \frac{1}{30} \sum_{\alpha,\beta} S_{\alpha\alpha,\beta\beta} \quad (5)$$

$$\delta_G = \frac{1}{30} \sum_{\alpha,\beta} S_{\alpha\beta,\alpha\beta} \quad (6)$$

$$\delta_H = \frac{1}{30} \sum_{\alpha,\beta} S_{\alpha\beta,\beta\alpha} \quad (7)$$

In order to compare the two-photon intensities with experimental data we convert the transition strengths (in a.u.) into cross sections given in the Göppert-Mayer unit; $1\text{GM} = 10^{-50} \frac{\text{cm}^4 \text{s}}{\text{photon}}$. The two-photon cross section for a given transition using two identical photons is expressed in the Göppert-Mayer unit by [39,40]

$$\sigma(\nu) = \frac{\pi^2 e^4}{c^2 \epsilon_0^2 h^2} \omega^2 g(\nu) \delta^{\text{TP}} = 4\pi^2 \alpha^2 \omega^2 g(\nu) \delta^{\text{TP}} \quad (8)$$

where α is the fine structure constant ($\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$) and $g(\nu)$ the band shape function, which is often represented by a GAUSSIAN profile.

For non-identical photons the conversion equation is similar to Eq. (8). However, the cross section at a given frequency becomes a sum of contributions from the GAUSSIAN profiles associated with all the transitions arising from using two photons of different energy. We have simplified this summation by assuming a box model instead of the GAUSSIAN profiles. For a given wavelength of the first photon we calculate the transition strength. We assume this strength to be constant within the box of width $\Delta\lambda$. The function $g(\nu)$ is in frequency space and we convert the box width to a frequency width ($\Delta\nu$). Since $g(\nu)$ is normalized, its height g_{max} is $\Delta\nu^{-1}$. This can be used in Eq. (8) to calculate a cross section value that can be used within the box.

We suggest that the J -value for two-photon transition to an excited state can be calculated in a manner similar to the one-photon expression by [41]

$$J = \int \int \sigma(\lambda_1, \lambda_2) F(\lambda_1) F(\lambda_2) \phi(\lambda_1, \lambda_2) d\lambda_1 d\lambda_2 \quad (9)$$

where λ_1 and λ_2 are the wavelengths of the two photons, $\sigma(\lambda_1, \lambda_2)$ is the wavelength dependent two-photon cross section given in the Göppert-Mayer unit, $F(\lambda)$ is the frequency dependent solar flux, and ϕ is the quantum yield. We integrate over the wavelength of the photons exciting the molecule, but the wavelength of the two photons depends on each other, since the sum of the energies of the two photons equal the excitation energy to a given electronic excited state. Thus in practice the double integral is only a single integral. In our calculations we sum the J -values for transitions to the eight lowest lying electronic states and we fix ϕ to 1. We use the TUV radiation model to calculate the solar flux from 120 to 800 nm [42]. The calculated flux is averaged over a 24 h period, for 26°N to 32°N, from April to May.

3. Results and discussion

It is generally known that diffuse basis functions are needed in order to describe electronic transitions [11,43]. We will use the AV(D + d)Z basis set for our calculations based on previous results. Lane et al. [11] showed that the AV(D + d)Z basis set performs almost as good as the AV(T + d)Z basis set in describing the one-photon electronic transitions in H₂SO₄, with an underestimation of less than 2% by CCSD/AV(D + d)Z with respect to CCSD/AV(T + d)Z in the vertical electronic excitation energies, and with an average variation of 25% in the oscillation strengths. The method and basis set dependence of two-photon intensities and energies in H₂SO₄ have also been investigated [44]. Changing from CCSD/V(D + d)Z to CCSD/V(T + d)Z creates a variation of 1–2% on excitation energies and 25% on transition strengths. We would expect a similar differences going from AV(D + d)Z to AV(T + d)Z as we find in going from V(D + d)Z to V(T + d)Z. No Rydberg character has been found for these low lying transitions and therefore no center of mass basis functions have been added [11].

In Table 1, two-photon intensities calculated with B3LYP and a hierarchy of coupled cluster quadratic response methods and the AV(D + d)Z basis set for the eight lowest energy excited states of H₂SO₄ are shown. $\delta_{\text{linear,parallel}}^{TP}$ refers to the fact that only linear parallel polarized photons contribute. The CCS method overestimates the excitation energies with a couple of eV, while the CC2 method underestimates it with about half an eV, both with respect to the CCSD method [12]. For the two-photon transition strengths, a similar convergence is found. The transition strengths changes by approximately 50%, from the CCS to the CC2 method and by about 30% from the CC2 to the CCSD method. The B3LYP method gives excitation energies that are about 1 eV lower than the CCSD values and for most states the B3LYP intensity is in reasonably agreement with the CCSD intensity. Based on these investigations, we conclude that CCSD combined with the AV(D + d)Z basis set provides a reasonable approach for our investigations.

3.1. Two-photon intensities

We have investigated how the transition strength of a two-photon transition depends on the wavelength of the photons absorbed. In Figure 1 we show the B3LYP/V(D + d)Z calculated transition strength of two photon excitation to the lowest lying A state in H₂SO₄. The transition strength is shown as a function of the wavelength of the first photon absorbed (λ_1), with the wavelength of the second photon (λ_2) defined such that the sum of energy of the two photons is the vertical excitation energy to the A state. The transition strength of a transition is independent of the order in which the photons are absorbed.

The wavelength of two equivalent photons required for excitation of this A state is $\lambda_1 = \lambda_2 \simeq 287$ nm. The photon flux drops very rapidly at wavelengths less than 200 nm and contribution to the

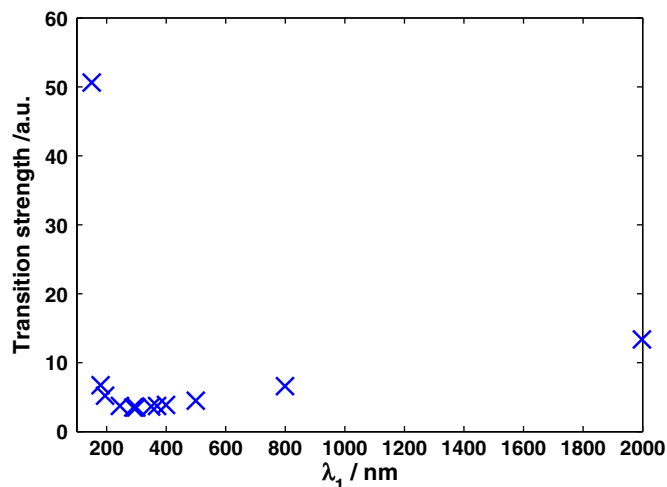


Figure 1. B3LYP/V(D + d)Z calculated two-photon transition strength for transition to the lowest lying A state in H₂SO₄ as a function of the wavelength of the first photon absorbed.

J -value that require one of the photons to have $\lambda \ll 200$ nm is likely to be very small. If $\lambda_1 = 200$ nm then $\lambda_2 = 506$ nm for two-photon excitation to this A state. Transition strengths with λ_1 in the range from about 180–700 nm is most relevant to estimate the J -value. In this range the transition strength lies within a factor of 6 for the eight excited states considered, with the variation mostly less than a factor of 2. The curves for transition to other electronic excited states look similar to that shown in Figure 1.

3.2. J -values

We calculate the J -value using Eq. (9) with the following approximations: the wavelength range of the first photon absorbed is limited to 170–700 nm and the transition strength is assumed constant in this range. We use the transition strength value calculated for two identical photons ($\lambda_1 = \lambda_2$) and use a box function instead of a GAUSSIAN function for $g(\nu)$. Within a box of width $\Delta\lambda$ the cross section is assumed constant with a value calculated from Eq. (8) and with the box width $\Delta\lambda$ converted to a width $\Delta\nu$ in units of s^{−1}. The conversion to frequency results in a variation in cross section $\sigma(\nu)$ with λ_1 despite a constant transition strength. In the range 170–700 nm this results in a factor of 16 variation in cross section with the cross section for two identical photons lying roughly in the middle. We have ignored this variation and assumed the cross section to be constant and have used the CCSD/AV(D + d)Z calculated value for two identical linear-parallel photons.

If we use the highest transition strength in the wavelength region 180–700 nm, instead of using the transition strength for two identical photons, this would increase the J -value with less than a factor of 6. In addition the upper limit on the error in the wavelength to frequency conversion is a factor of 5. Thus an upper limit on our values would be a factor of 30 higher than the values we present. The box size chosen had little effect on the results, with a change of box size from 1 to 2 nm resulting in a less than one percent change in the J -value.

In Table 2, the calculated J -values for one- and two-photon transitions of H₂SO₄, at altitudes of 30 and 100 km, are presented. The previously calculated [11] J -values corresponding to OH-stretching overtone induced photodissociation (visible), photodissociation in the UV region (UV) and photodissociation by Lyman- α photons (Lyman- α) are compared with the present two-photon J -values in Table 2. Despite the mentioned approximations it is clear that

Table 1

Calculated two-photon linear parallel transition strengths (in a.u.) and vertical excitation energies (in eV) for the eight lowest lying electronic excited states of H₂SO₄. The calculations have been carried out with the aug-cc-pV(D + d)Z basis set.

State	$\delta_{\text{linear,parallel}}^{TP}$				Energy
	B3LYP	CCS	CC2	CCSD	
1A	0.976	2.209	1.318	1.494	8.66
2A	6.330	3.928	12.054	6.300	9.21
3A	15.83	10.225	22.249	19.38	9.26
4A	23.46	4.594	19.455	9.830	10.02
1B	0.056	0.519	0.378	0.516	8.24
2B	4.325	1.435	4.343	2.623	8.35
3B	2.297	0.928	2.793	2.165	9.69
4B	5.564	3.143	4.471	2.453	10.07

Table 2

J -values (s^{-1}) for different photodissociation mechanisms of H_2SO_4 at altitudes of 30 and 100 km.

Altitude	J value (s^{-1})			
	Visible [11]	UV [11]	Lyman- α [11]	Two-photon
30 km	5.5×10^{-8}		2.9×10^{-13}	3.8×10^{-25}
100 km	5.8×10^{-8}	9.8×10^{-9}	9.0×10^{-6}	1.1×10^{-23}

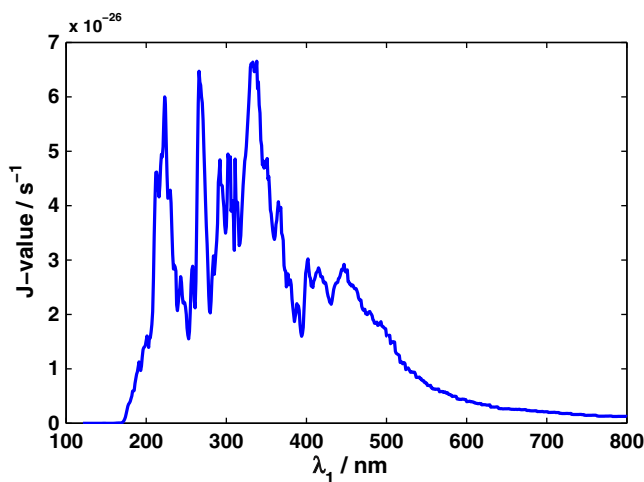


Figure 2. Calculated J -value contribution for two-photon photodissociation of H_2SO_4 at 100 km as a function of the wavelength of the first photon absorbed.

the contribution to the J -value from two-photon excitations is insignificant. The two-photon mechanism will not even compete with low lying one-photon electronic transitions in the UV region, which have already been concluded not to contribute to the photodissociation of H_2SO_4 at any altitude [11,14]. The two-photon J -value increases almost two orders of magnitude going from 30 to 100 km, due to the altitude dependency of the solar flux in the UV region, but is still of no significance.

In Figure 2 we present the contributions to the J -value in the wavelength region 170–700 nm at an altitude of 100 km. This clearly illustrates the wavelength region of importance. The contribution from each of the eight electronic states considered are within two orders of magnitude of each other. The dominant contributions arise from transitions to the 3A and 2B states. At 100 km the maximum contribution is $4.3 \times 10^{-24} s^{-1}$ (2B) and it is unlikely that adding additional electronic excited states will change the total J -value significantly compared with the J -values of the other processes.

In our calculations of the two-photon J -values, we assume that all the solar photons are linear parallel orientated. However, the atmosphere does not only contain those photons, but instead photons with all kinds of orientations. Furthermore, we have not included a factor that take the possibility of two photons with a specific orientation and energy to be absorbed at the same time, into account. Thus our calculated two-photon J -values are not accurate, but do provide a reasonable estimate. Our results emphasize the fact, that two-photon excitation of H_2SO_4 does not contribute to the dissociation of H_2SO_4 in the atmosphere.

4. Conclusions

We have calculated two-photon electronic transitions in H_2SO_4 using a hierarchy of coupled cluster response methods and correlation consistent basis sets. Based on these results we have investigated the frequency dependency of the two-photon transition

strengths. We find that the transition strengths are more or less constant in the wavelength area of interest. We have estimated two-photon J -values for altitudes of 30 and 100 km, and find those to be in the order of $10^{-25} s^{-1}$ and $10^{-23} s^{-1}$, respectively. Finally we conclude that two-photon excitation of H_2SO_4 at no altitude will contribute to photodissociation of H_2SO_4 .

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