Infrared transitions probabilities and radiative opacity of SiO

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Abstract. Spectroscopic properties of SiO have been calculated from highly correlated wave functions. The computed dipole moments for $v = 0 - 3$ agree well with the experimental data of Raymonda et al. (1970). By comparing the present results with previous theoretical works, we estimate that the resulting line strengths should be the most accurate to date. The Einstein coefficients for the fundamental and the first overtone ($v \leq 40$, $J \leq 100$) are larger than the currently used values of Tipping & Chackerian (1981), and should be tested in models of stellar atmospheres.

Key words: infrared: general – molecular data – stars: AGB and post-AGB – ISM: molecules

1. Introduction

The silicon monoxide molecule is of considerable astrophysical interest. SiO has been identified in sunspot spectra (Gaur et al. 1972, 1978). The pure rotational radiofrequency spectrum was first observed from the interstellar medium (Wilson et al. 1971) and the discovery of maser emission from the Orion nebula (Snyder & Buhl 1974) has encouraged a systematic search for SiO in various stellar and interstellar sources (Geballe & Townes 1974, Kwan & Scoville 1974, Elitzur 1980). The $\Delta v = 1$ and 2 transitions in the electronic ground state have been observed in absorption in the infrared spectra of circumstellar atmospheres or the photosphere of cool stars (Rinsland & Wing 1982, Cohen et al. 1992).

Very accurate molecular constants for the $X^1\Sigma^+$ ground state are available from millimeter wave (Manson et al. 1977, Mollaaghababa et al. 1991) and from IR spectra (Campbell et al. 1995). But a quantitative interpretation of astrophysical spectra requires in addition accurate oscillator strengths for the vibration-rotation observed transitions. Various experimental and theoretical papers have been devoted to this problem. The only experimental study dealing with the dipole moment of SiO has been reported by Raymonda et al. (1970) who accurately measured the dipole moment and its derivative

at the equilibrium distance of the SiO molecule. Using these experimental data and the long range values of the theoretical dipole moment function obtained by Langhoff & Arnold (1979), Tipping & Chackerian (1981) have built an electric dipole moment function (EDMF) in the form of a Padé approximant to obtain transition probabilities for a large number of rovibrational transitions. Since this work, there have been several theoretical calculations of the dipole moment function of SiO at different levels of electronic correlation (Werner et al. 1982, Botschwina & Rosmus 1985, Peterson & Woods 1990, Langhoff & Bauschlicher 1993 (LB)). All the theoretical results differ significantly from the results of Tipping & Chackerian (1981) (TC). Finally, recent observations of the infrared spectra of Alpha Tau suggest values of line strengths much larger than TC values (LB) . It therefore seemed useful to us to reinvestigate the determination of the dipole moment function of SiO, and then deduce transition probabilities and infrared radiative opacities of this molecule.

2. Summary of calculation

The Gaussian basis sets employed are general contractions based on atomic natural orbitals. The primitive basis set for silicon comprises the [20s,12p] set of Woon & Dunning (1993) contracted to [7s, 6p] and the [4d, 3f, 2g, 1h] functions of Dunning (1989). This set was augmented by diffuse functions with exponents .028 (s) and .021 (p). For oxygen, the basis set comprises the [14s, 8p] set of Dunning (1989) contracted to [6s, 5p] and [4d, 3f, 2g, 1h) polarization functions. This set was augmented by two diffuse functions with exponents .073 (s) and .049 (p). The total number of contracted Gaussian functions was 194.

Two types of calculations have been performed. First, in the region close to the equilibrium distance, the dominant configuration ($7\sigma^2 2\pi^4$) has a weight larger than .9 and thus a single reference based coupled-cluster singles and doubles method (Bartlett 1981) including a perturbational correction for triple excitation (CCSD(T)) is very well adapted. To obtain the general behavior of the potential energy and dipole moment fuctions, multireference configuration interaction (MRCI) wave functions were constructed using multiconfiguration self-consistent
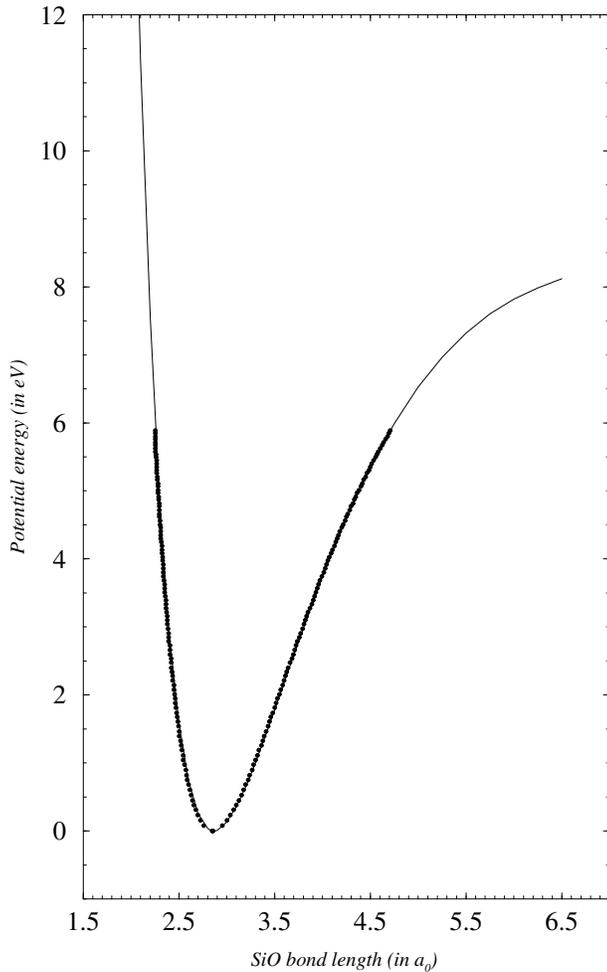
Fig. 1. Comparison of the MRCI potential with the RKR curve for the $X^1\Sigma^+$ state of the SiO molecule (this work: solid line, RKR: plain circles
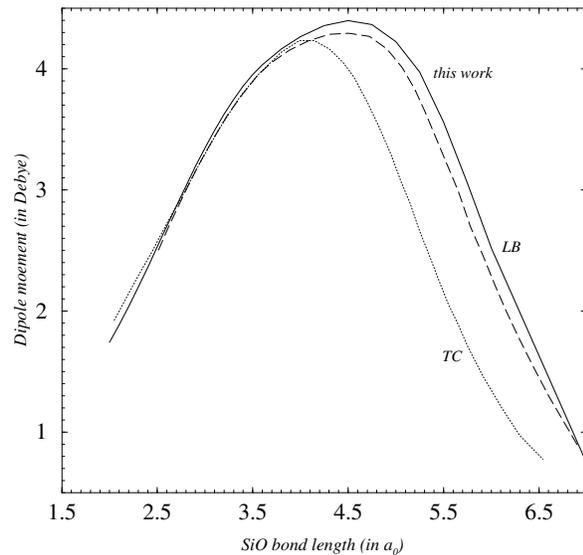

Fig. 2. Dipole moment functions for the $X^1\Sigma^+$ state of SiO. The solid and the dashed lines denote the present work (MRCI) and the ACPF results (LB) respectively, the dotted line is from TC.

field (MCSCF) active space (Werner & Knowles 1985,1988, Knowles & Werner 1985, 1988) with valence and Rydberg orbitals ($5\sigma - 10\sigma, 2\pi - 4\pi$). All valence electrons, including the oxygen 2s electrons whose importance was pointed out by LB, were correlated. The reference space was restricted to include only occupations for which the absolute value of any determinant exceeded 0.01 for all distances between 2 and 10 $a_0 (a_0 = .529177\text{Å})$. The MRCI wave functions accounted for more than 75 millions of configurations which were internally contracted to 3 millions of configurations. All the calculations have been performed with the MOLPRO code[1].

The calculated potential curve compares very well (Fig. 1) with the RKR curve (Campbell et al. 1995), particularly in the region close to the equilibrium distance. The derived spectroscopic constants are compared with previous ab initio work and

experiment in Table 1. The CCSD(T) calculated dissociation energy (D_e) is in quantitative agreement with the experimental value and the high quality of the present results is given by the comparison of the computed and the measured spectroscopic parameters $R_e, \omega_e, \omega_e x_e$. In particular, the CCSD(T) and MRCI potentials have an error of $10^{-2}a_0$ in R_e and give energy differences between any vibrational level v and $v = 0$ accurate to within 5cm^{-1} up to $v = 20$. Thus, the accuracy of the calculated transition probabilities and Einstein coefficients will depend only on the accuracy of the EDMF.

No direct measurement of Einstein coefficients is available. Our MRCI dipole moment function is compared in Fig. 2 with the most recent theoretical results (LB) and with the function constructed by TC in the form of a Padé approximant which reproduces the experimental values of Raymonda et al. (1970) and fits the calculated values of Langhoff et Arnold (1979) (LA) at large internuclear distances R.

The three theoretical curves are very similar close to the equilibrium distance but differ signicantly at large internuclear distance with the results of Tipping et Chackerian (1981).The curve obtained with the CCSD(T) method for $R \leq 4a_0$ is indistinguishable from the MRCI results at the scale of Fig. 2.

All curves are practically linear in the region $v = 0$ to $v = 4$. The slope of the dipole moment function at R_e, equal to 0.629 D and 0.593 D for the MRCI and CCSD(T) calculations must be compared to the experimental value of 0.523 ± 0.107. It decreases with higher level of correlation as was previously discussed by LB, so that the CCSD(T) moment which takes into account the major part of the electronic correlation must be considered as the most accurate of our two results near R_e. Using the CCSD(T) dipole moment for low values of R distances and the MRCI values for larger values and the MRCI potential at

Table 1. Calculated and experimental spectroscopic constants for $^{28}Si^{16}O$

Method	Reference	R_e in (a_0)	ω_e (cm^{-1})	$\omega_e x_e$	D_e (cm^{-1})
CCSD(T)	this work	2.864	1242.0	6.25	66526
MRCI	this work	2.864	1240.2	6.30	67303
SCF+CI	Langhoff & Arnold 1979	2.827	1248	5.92	65334
MCSCF+CI	Werner et al. 1982	2.863	1284	5.8	
CEPA	Botschwina & Rosmus 1985	2.871	1241	5.95	
EXP	Campbell et al. 1995	2.853	1241.5	5.97	66620 ± 1049

Table 2. Dipole moments (in Debye) and dipole derivatives $d\mu/dR$ and $d^2\mu/dR^2 \mid_{R_e}$ (in ua) at the equilibrium distance.

	this work	LA	BR	LB	TC	Raymonda et al.(1970)
method	MRCI+CCSD(T)	SCF+CI	CEPA	ACPF	Padé	exp
$v = 0$	3.0869	3.106	3.067	3.0436	3.0982	3.0981
$v = 1$	3.1089	3.124	3.086	3.0639	3.1178	3.1177
$v = 2$	3.1297	3.143	3.103	3.0836	3.1372	3.1372
$v = 3$	3.1537	3.160	3.121	3.1028	3.1568	3.1573
$d\mu/dR$	0.593	0.571	0.591	0.613	0.5367	0.523 ± 0.107
$d^2\mu/dR^2 \mid_{R_e}$	0.127	0.151	0.151	-	0.0357	0.0 ± 0.331

all internuclear distances, we have calculated dipole moments averaged in the $v = 0 - 3$ vibrational levels. These results are compared in Table 2 with the best ab initio theoretical values and with the experiment of Raymonda et al. (1970). All theoretical results are comprised in the error bars of the experiment. The best agreement with the mean value is obtained with our result (accuracy better than .01 Debye). Obviously, the dipole moment of TC obtained by a fitting procedure for these four vibrational levels agrees very well with the experimental results, but its validity for higher vibrational levels is questionable, due to the form of the Padé approximant which fits at large values the results of LA. As discussed by several authors, these theoretical results, accurate near the equilibrium distance, do not take into account some electronic configurations which are important at large distances. On the whole, our ab initio results which show simultaneous accuracy of both the potential and the dipole moment function and its derivatives must be considered as the most accurate ab initio result to date. We estimate that the resulting theoretical line strengths should be accurate to 20% for the fundamental band.

3. Einstein coefficients and infrared opacities

The band transition probabilities between the vibrational wave functions $\mid v' \rangle$ and $\mid v'' \rangle$ are expressed in terms of Einstein coefficients $A_{v'v''}$:

$$A_{v'v''}(s^{-1}) = (64\pi^4 \nu_{v'v''}^3/3h) \mid \langle v' \mid M(R) \mid v'' \rangle \mid^2 \qquad (1)$$

where $\nu_{v'v''}$ is the frequency in cm^{-1} of the transition, $M(R)$ is the electric dipole moment function. The vibra-

tional wave functions are obtained from solutions of the vibrational Schrödinger equation using standard numerical integration methods (Huré & Roueff 1993). Einstein coefficients for the fundamental band and the first overtone are compared in Table 3 with the results of TC. The agreement is relatively good for $\Delta v = -1$ transitions, but our results are larger by a factor ≈ 1.3 for $\Delta v = -2$ transitions. This is mainly due to a difference in the second derivative $d^2\mu/dR^2 \mid_{R_e}$ of the dipole moment function, which is difficult to deduce accurately from the experiment (cf Table 2). As noticed by Werner et al. 1982, the shape of the transition moment function with a maximum close to the equilibrium distance leads to intense overtone transitions as can be seen in Fig. 3 where we have drawn, for equal initial populations, the emission intensities for the fundamental, first and second overtone bands up to $v = 40$. Of course, the relative intensities of the overtones relative to the fundamental band decrease when the Boltzmann factor is taken into account (see for example Fig. 4 for $T = 5000K$).

SiO is a major source of absorption in the atmosphere of many late-type stars and circumstellar media (Cohen et al. 1992, and references therein), but no opacity data are available involving high excited rovibrational states. We have thus calculated the temperature-dependent absorption coefficient or opacity $K(\nu, T)$ (cm^2 per molecule).

If we consider a rovibrational transition $v''J'' \to v'J'$ occuring in the absorption of a photon ν close to $\nu_0 = (E_{v'J'} - $
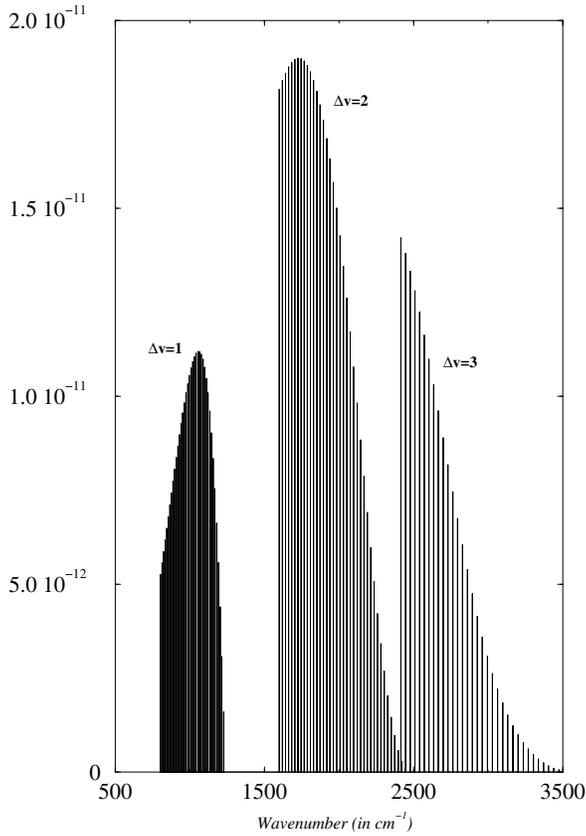
Fig. 3. Infrared emission intensities ($Ahc\nu$ in erg s^{-1}) of $^{28}Si^{16}O$ calculated up to $v = 40$ ($J' = 0$) with equal initial populations versus wavenumber (in cm^{-1}).

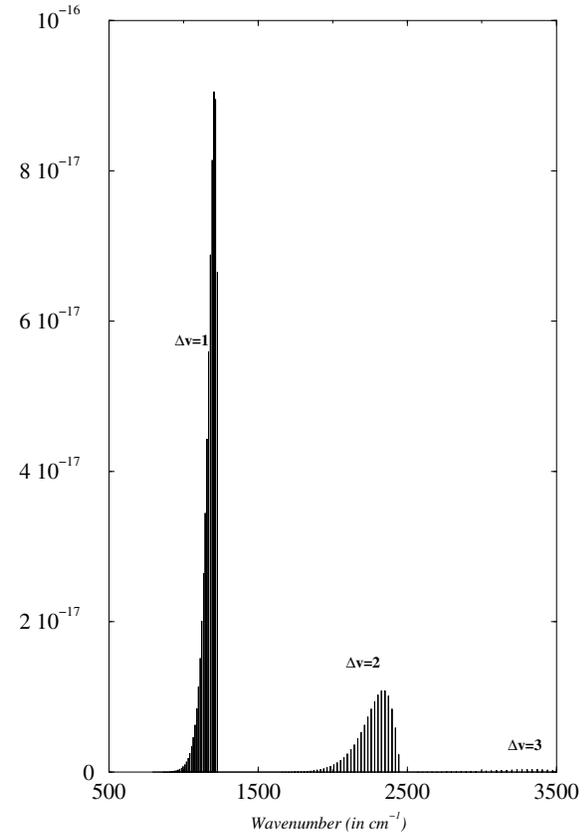**Table 3.** Einstein coefficients (s^{-1}) for the fundamental and the first overtone bands ($J'' = 1$ and $J' = 0$)

$v' - v''$	this work	TC
$1 - 0$	6.61	5.16
$2 - 1$	12.73	10.02
$3 - 2$	18.40	14.58
$4 - 3$	23.57	18.83
$2 - 0$	0.17	0.14
$3 - 1$	0.60	0.40
$4 - 2$	1.21	0.80
$5 - 3$	2.07	1.31

$E_{v''J''})/hc$, the absorption cross section $\sigma(\nu)$ is related to the oscillator strength $f_{v''J''}^{v'J'}$ by:

$$\sigma(\nu) = \frac{\pi e^2}{mc^2} f_{v''J''}^{v'J'} \phi(\nu) \qquad (2)$$

where $\phi(\nu)$ is the normalized profile of the transition.

The temperature-dependent absorption coefficient is given by:

$$K(\nu, T) = \sigma(\nu) \frac{N_{v''J''}}{N_{Tot}} \qquad (3)$$

Fig. 4. Infrared emission intensities ($Ahc\nu$ in erg s^{-1}) of $^{28}Si^{16}O$ calculated up to $v = 40$ ($J' = 0$) for temperature $T = 5000K$ versus wavenumber (in cm^{-1}).

where $N_{v''J''}$ is the population of the absorbing initial level and N_{Tot} the total population of the molecule. Assuming LTE for the level populations and introducing stimulated emission, we obtain:

$$K(\nu, T) = \frac{\pi e^2}{mc^2} f_{v''J''}^{v'J'} \phi(\nu) \frac{2J'' + 1}{Q_{int}} \exp(-\frac{\Delta E_{v''J''}}{kT})$$
$$(1 - \exp(-\frac{hc\nu}{kT})) \qquad (4)$$

where Q_{int} is the internal partition function (Sauval & Tatum 1984) and $\Delta E_{v''J''}$ is the energy difference between the absorbing level and the ground $(0,0)$ level. In the case of a pure Doppler broadening, the line shape is gaussian and as long as thermal motions dominate line broadening, the absorption profile can be replaced by a rectangle centered at ν_0 with a width $\Delta\nu_{FWHM} = 2\sqrt{ln2}\Delta\nu_D$, where

$$\Delta\nu_D = \frac{\nu_0}{c} \sqrt{\frac{2kT}{M(SiO)}} \qquad (5)$$

The absorption spectrum is very sparse over the considered spectral range and the line spacing is always larger than the Doppler width. We thus divide the IR spectral range in intervals
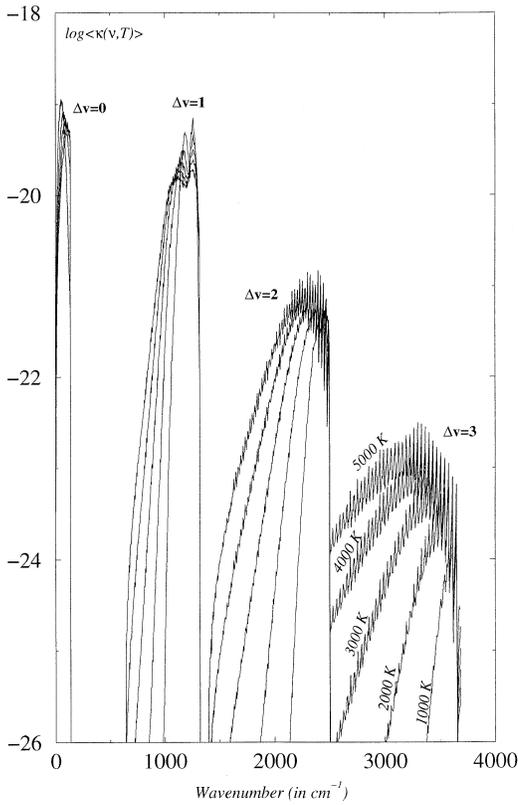
Fig. 5. Logarithm of the radiative opacity (in cm^2 per molecule) of $^{28}Si^{16}O$ versus wavenumber (in cm^{-1}) for $T = 1000, 2000, 3000, 4000, 5000 K$.

of constant width $\Delta\nu_{SM}$ and define a "Straight Mean" opacity by summing the integrated absorption coefficients for each line which falls into a given interval and dividing by the corresponding width (Tsuji, 1966). For a given interval number k the mean opacity is thus given by:

$$\langle K(T)_k \rangle = \frac{1}{\Delta\nu_{SM}} \sum_{lines} [K(\nu, T)\Delta\nu_{FWHM}] \tag{6}$$

We have calculated the mean opacities with $\Delta\nu_{SM} = 5 cm^{-1}$ for 5 different temperatures: 1000K, 2000K, 3000K, 4000K, 5000K (see Fig. 5), taking into account vibrational levels up to 40, with a maximum for J' values of 100. The successive vibrational sequences appear successively with increasing wavenumber. These data give a very convenient way to estimate the IR absorption of SiO in environments where LTE is valid. Extensive numerical data are available upon request.

4. Conclusions

The present calculations of the potential energy function and the dipole moment of the $X^1\Sigma^+$ state of SiO have been used to obtain Einstein coefficients for vibrational transitions in the ground state and IR opacities. The results agree well with the experimental data of Raymonda et al. (1970) for $v = 0 - 3$ and

an extensive comparison with previous ab initio calculations allows us to conclude that the permanent dipole moment for these vibrational levels has been determined to better than 1% accuracy. The Einstein coefficients for rovibrational transitions are larger than the currently used values of Tipping & Chackerian (1981), and should be tested in models of stellar atmospheres in conjunction with high resolution observations of the first overtone. Our ab initio data display an actual improvement. Moreover, new experimental measurements for the dipole moment in higher vibrational states should be very useful. Infrared data are available at the Centre de Données de Strasbourg.

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