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# Ab initio CI calculation of single vibronic level fluorescence emission spectra and absolute radiative lifetimes of H<sub>2</sub>CO (<sup>1</sup>A<sub>2</sub>)

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Overlap integrals and dipole transition moments which were obtained by an *ab initio* CI calculation are used for the calculation of fluorescence emission spectra and absolute radiative lifetimes of single vibronic levels of H<sub>2</sub>CO (<sup>1</sup>A<sub>2</sub>). The agreement between calculation and experiment is fairly good. The analysis of the results shows that a large fraction of the total emission intensity is due to low-intensity transitions and bands at wavelengths larger than 460 nm. The implications of this result for the determination of fluorescence quantum yields and radiative lifetimes are discussed.

## I. INTRODUCTION

The radiative transition between two single vibronic levels (SVL) of the electronic ground and first excited state of formaldehyde is described<sup>1</sup> by the total dipole transition moment *D*:

$$D = \prod_{n \neq k} \langle \chi_{0q}(Q_k) | D(Q_k) | \chi_{1p}(Q_k) \rangle_{Q_k} \langle \chi_{0q}(Q_n) | \chi_{1p}(Q_n) \rangle_{Q_n}, \quad (1)$$

where *D*(*Q*<sub>*k*</sub>) is the electronic dipole transition moment, which induces the transition;  $\chi_{0q}(Q_k)$  is the *q*th vibrational wave function of normal mode *k* in the ground state, and  $\chi_{1p}(Q_k)$  is the *p*th vibrational wave function of normal mode *k* in the first excited state. The subscript *Q*<sub>*k*</sub> denotes integration over normal coordinate *Q*<sub>*k*</sub>, and the product runs over the normal coordinates. In a recent paper,<sup>1</sup> hereafter to be denoted as Paper I, we published all the integrals occurring in Eq. (1) and calculated from them the "cold" (*nπ\**) absorption spectrum, i. e., the absorption spectrum resulting from the vibrationless ground state level. The potential energy surfaces, which determine the vibrational wave functions, were obtained from an *ab initio* CI calculation; the anharmonic vibrational wave functions themselves were numerically determined on these potential energy surfaces. The most important quantities in Eq. (1), the electronic dipole transition moments *D*(*Q*<sub>*k*</sub>), were explicitly calculated as functions of the nuclear geometry. Throughout the calculation we used the dipole length expression for *D*(*Q*<sub>*k*</sub>):<sup>1</sup>

$${}^L D(Q_k) = \left\langle \phi_1 \left| \sum_i q_i \phi_0 \right. \right\rangle_q,$$

where  $\phi_0$  and  $\phi_1$  are the electronic ground and first excited state, respectively; *q*<sub>*i*</sub> stands for the Cartesian coordinates of electron *i*.

In Paper I, we showed that for the description of radiative transitions, the dipole length expression is superior to the dipole acceleration form of the electronic transition moment. Every nuclear geometry used in the calculation gives a *D*(*Q*<sub>*k*</sub>) value; cubic spline func-

tions are fitted to these values and the result is substituted in Eq. (1).

From the integrals obtained in this way, it is also possible to calculate the fluorescence emission spectrum resulting from a SVL in H<sub>2</sub>CO(<sup>1</sup>A<sub>2</sub>); a calculation completely analogous to the one given in Paper I for the cold absorption spectrum.

The intensities of the various transitions are proportional to the oscillator strengths,

$$f = \frac{2}{3} \Delta E |D|^2,$$

where *D* is the total dipole transition moment from Eq. (1) and  $\Delta E$  is the energy corresponding to the transition. Very recently,<sup>2</sup> Shibuya, Harger, and Lee published for the first time the intensity distribution of the fluorescence emission spectra of two SVL of H<sub>2</sub>CO(<sup>1</sup>A<sub>2</sub>): 4<sup>0</sup> and 4<sup>1</sup>. In this paper, we give the results of the calculation of the theoretical spectra in order to investigate, to what extent the integrals given in Paper I can be used for predicting fluorescence spectra from other SVL and for interpreting experimental results.

It is also possible<sup>3</sup> to calculate from the obtained *D* values the total radiative lifetime  $\tau_r$  of a SVL:

$$\tau_r^{-1} = \frac{4}{3c^3} \sum (\Delta E)^3 |D|^2, \quad (2)$$

where *c* is the velocity of light (= 137 a. u.), and the summation is over all possible transitions from the SVL in question. Although this  $\tau_r$  value, being the combined result of a large number of transitions, is a much less refined quantity to characterize the radiative properties of a SVL than its fluorescence emission spectrum, it is worth calculating  $\tau_r$  because for most SVL of formaldehyde  $\tau_r$  values are known experimentally<sup>4</sup> contrary to the fluorescence spectra.

## II. RESULTS AND DISCUSSION

### A. Fluorescence emission spectra

In Table I, we give the calculated oscillator strengths of the most intensive bands<sup>5</sup> occurring in the 4<sup>1</sup> and 4<sup>0</sup> fluorescence emission spectra for wavelengths smaller than about 460 nm, being the region for which the ex-

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TABLE I. Calculated oscillator strengths of the most intensive bands in the 4<sup>1</sup> and 4<sup>0</sup> fluorescence emission spectra.

4 <sup>1</sup> Spectrum			4 <sup>0</sup> Spectrum		
Transition	$\Delta E$ (cm <sup>-1</sup> )	$f \times 10^6$ (a. u.)	Transition	$\Delta E$ (cm <sup>-1</sup> )	$f \times 10^6$ (a. u.)
4 <sub>0</sub> <sup>1</sup>	28 313	3.4	4 <sub>1</sub> <sup>0</sup>	27 021	18.0
3 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	26 812	0.6	4 <sub>0</sub> <sup>0</sup> 6 <sub>1</sub> <sup>0</sup>	26 937	1.0
2 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	26 566	7.6	3 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	25 520	3.1
4 <sub>2</sub> <sup>1</sup>	26 061	26.6	4 <sub>0</sub> <sup>0</sup> 5 <sub>1</sub> <sup>0</sup>	25 345	1.3
4 <sub>1</sub> <sup>1</sup> 6 <sub>1</sub> <sup>0</sup>	25 894	0.8	2 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	25 275	40.3
2 <sub>1</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	25 066	1.3	2 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 6 <sub>1</sub> <sup>0</sup>	25 191	2.3
2 <sub>2</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	24 820	8.8	4 <sub>3</sub> <sup>0</sup>	24 686	18.9
3 <sub>1</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	24 560	4.6	4 <sub>2</sub> <sup>0</sup> 6 <sub>1</sub> <sup>0</sup>	24 602	0.5
4 <sub>1</sub> <sup>1</sup> 5 <sub>1</sub> <sup>0</sup>	24 302	0.9	1 <sub>1</sub> <sup>0</sup> 4 <sub>4</sub> <sup>0</sup>	24 254	0.5
2 <sub>1</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	24 232	59.5	3 <sub>2</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	24 020	0.3
2 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>1</sup> 6 <sub>1</sub> <sup>0</sup>	24 148	1.7	3 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 5 <sub>1</sub> <sup>0</sup>	23 844	0.2
1 <sub>1</sub> <sup>0</sup> 2 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	23 800	0.2	2 <sub>1</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	23 774	7.0
4 <sub>4</sub> <sup>1</sup>	23 643	27.1	2 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 5 <sub>1</sub> <sup>0</sup>	23 599	2.9
4 <sub>3</sub> <sup>1</sup> 6 <sub>1</sub> <sup>0</sup>	23 560	0.6	2 <sub>2</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	23 529	45.8
2 <sub>2</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	23 320	1.5	2 <sub>2</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 6 <sub>1</sub> <sup>0</sup>	23 445	2.6
1 <sub>1</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	23 292	0.7	3 <sub>1</sub> <sup>0</sup> 4 <sub>3</sub> <sup>0</sup>	23 313	3.3
2 <sub>3</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	23 074	6.3	2 <sub>1</sub> <sup>0</sup> 4 <sub>3</sub> <sup>0</sup>	23 068	42.3
3 <sub>2</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	23 060	0.4	4 <sub>2</sub> <sup>0</sup> 5 <sub>1</sub> <sup>0</sup>	23 010	0.7
2 <sub>1</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	22 814	10.3	2 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 6 <sub>1</sub> <sup>0</sup>	22 856	1.2
2 <sub>1</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>1</sup> 6 <sub>1</sub> <sup>0</sup>	22 647	0.3	4 <sub>5</sub> <sup>0</sup>	22 352	9.9
2 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>1</sup> 5 <sub>1</sub> <sup>0</sup>	22 556	2.1	2 <sub>2</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	22 028	7.9
2 <sub>2</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	22 486	67.4	2 <sub>2</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 5 <sub>1</sub> <sup>0</sup>	21 853	3.2
2 <sub>2</sub> <sup>0</sup> 4 <sub>1</sub> <sup>1</sup> 6 <sub>1</sub> <sup>0</sup>	22 402	1.9	2 <sub>3</sub> <sup>0</sup> 4 <sub>1</sub> <sup>0</sup>	21 782	33.3
3 <sub>1</sub> <sup>0</sup> 4 <sub>4</sub> <sup>1</sup>	22 143	4.7	2 <sub>2</sub> <sup>0</sup> 4 <sub>0</sub> <sup>0</sup> 6 <sub>1</sub> <sup>0</sup>	21 699	1.9
1 <sub>1</sub> <sup>0</sup> 2 <sub>2</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	22 054	0.2	2 <sub>1</sub> <sup>0</sup> 4 <sub>2</sub> <sup>0</sup> 5 <sub>1</sub> <sup>0</sup>	21 264	1.4
4 <sub>3</sub> <sup>1</sup> 5 <sub>1</sub> <sup>0</sup>	21 967	0.8			
2 <sub>1</sub> <sup>0</sup> 4 <sub>4</sub> <sup>1</sup>	21 897	60.2			
2 <sub>1</sub> <sup>0</sup> 4 <sub>3</sub> <sup>1</sup> 6 <sub>1</sub> <sup>0</sup>	21 813	1.4			
2 <sub>3</sub> <sup>0</sup> 3 <sub>1</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	21 574	1.1			
1 <sub>1</sub> <sup>0</sup> 2 <sub>1</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	21 549	1.6			
2 <sub>4</sub> <sup>0</sup> 4 <sub>0</sub> <sup>1</sup>	21 328	3.1			
2 <sub>1</sub> <sup>0</sup> 3 <sub>2</sub> <sup>0</sup> 4 <sub>2</sub> <sup>1</sup>	21 314	0.9			
4 <sub>6</sub> <sup>1</sup>	21 309	10.7			

perimental spectra<sup>2</sup> are known. For the most intensive transitions we compare in Fig. 1 in a graphical way the experimental<sup>2</sup> intensity distribution with the calculated oscillator strengths. From the results we can see that in general the agreement between experiment and calculation is quite satisfactory. We have taken the intensities relative to the 2<sub>1</sub><sup>0</sup>4<sub>2</sub><sup>1</sup> transition because a relatively large discrepancy between calculation and experiment occurs for the 4<sub>2</sub><sup>1</sup> transition, which was used by Shibuya *et al.*<sup>2</sup> as reference.

As an illustration for the application of the calculated

oscillator strengths, we mention that Shibuya *et al.*<sup>2</sup> worried about the possibility that 2<sub>m-1</sub><sup>0</sup>4<sub>1</sub><sup>1</sup>5<sub>1</sub><sup>0</sup> transitions might be overlapped by 2<sub>m-1</sub><sup>0</sup>4<sub>1</sub><sup>1</sup>5<sub>1</sub><sup>0</sup>. From the  $f$  values given in Table I it is seen that the intensities of 2<sub>m-1</sub><sup>0</sup>4<sub>1</sub><sup>1</sup>5<sub>1</sub><sup>0</sup> are much lower than the ones of 2<sub>m</sub><sup>0</sup>4<sub>2</sub><sup>1</sup>. We find that the ratio 4<sub>1</sub><sup>1</sup>5<sub>1</sub><sup>0</sup>/2<sub>1</sub><sup>0</sup>4<sub>2</sub><sup>1</sup> = 0.016, and 2<sub>1</sub><sup>0</sup>4<sub>1</sub><sup>1</sup>5<sub>1</sub><sup>0</sup>/2<sub>2</sub><sup>0</sup>4<sub>2</sub><sup>1</sup> = 0.031, so this overlap can be neglected. The same holds for the possible overlap of 2<sub>m</sub><sup>0</sup>4<sub>2</sub><sup>1</sup> by 2<sub>m</sub><sup>0</sup>4<sub>1</sub><sup>1</sup>6<sub>1</sub><sup>0</sup>. The broken lines in Fig. 1 are transitions, which are experimentally not reported, but which have, according to Table I, oscillator strengths comparable with the 2<sub>m</sub><sup>0</sup>4<sub>0</sub><sup>1</sup> transitions (the measured transitions with the lowest intensities). These unre-

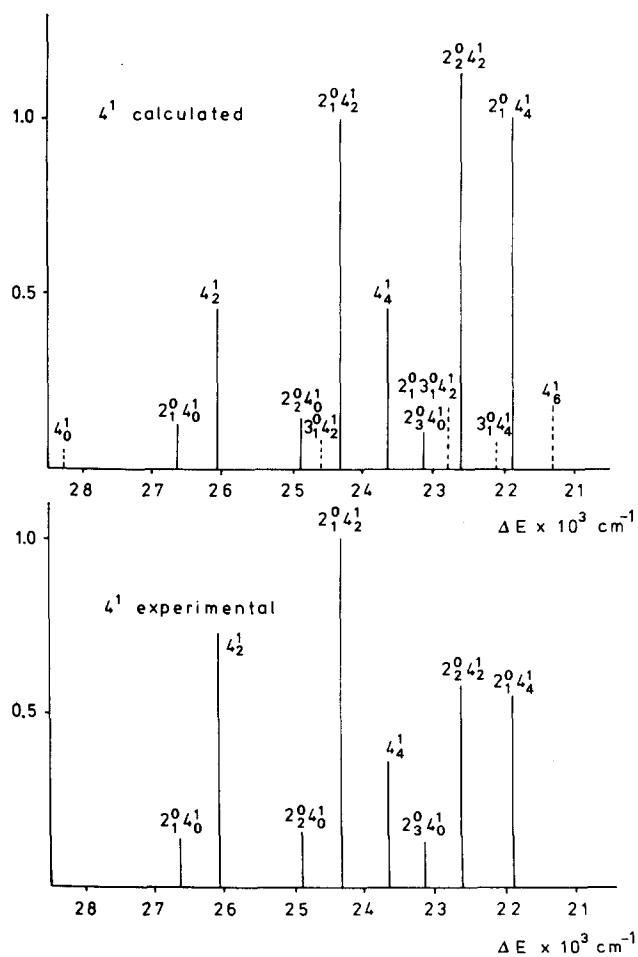


FIG. 1. Calculated and experimental<sup>2</sup> fluorescence emission spectra from the  $4^1$  level. The intensities are relative to the  $2_1^0 4_2^1$  transition. The broken lines are the highest calculated intensities, which are experimentally not found.

ported transitions should, according to the calculation, be measurable.

The low intensity bands, given in Table I, give rise to a low "background" emission spectrum with, owing to the increasing number of bands, an intensity slowly increasing with the wavelength. As will be seen in Sec. II. B, these small bands represent a nonnegligible part of the total emission intensity. For the  $2_2^0 4_2^1$  and  $2_1^0 4_4^1$  transitions, both lying in the region where the experimental determinations become more difficult because of spectral congestion, there is a relatively large difference between experiment and calculation. We note, that the experimental intensity behavior is peculiar for these bands: theoretically, the ratio  $R = D^2(2_2^0 X_B^A) / D^2(2_1^0 X_B^A)$  is 1.22 for all  $X_B^A$ . For  $X_B^A = 4_0^1$  the experimental value<sup>2</sup> follows the theoretical prediction:  $R = 1.31 \pm 0.62$ . For  $X_B^A = 4_2^1$ , however, the experimental intensities<sup>2</sup> result in  $R = 0.63 \pm 0.10$ , which is far out of the expected range. Also, the  $2_1^0 4_4^1$  transition is experimentally lower than expected.

In Fig. 2, we compare the experimental<sup>2</sup> and calculated  $4^0$  fluorescence emission spectra. Most of the remarks made for the  $4^1$  spectrum apply here too: Table I shows that the overlap of  $2_m^0 4_1^0$  by  $2_{m-1}^0 5_1^0$  or  $2_m^0 6_1^0$

is negligible; the transitions, indicated in Fig. 2 by broken lines, should be detectable and the experimental intensity ratios  $2_2^0 4_1^0 / 2_1^0 4_1^0$  and  $2_1^0 4_3^0 / 4_3^0$  are lower, than is expected on theoretical grounds. The large number of low intensity bands gives rise again to a low background emission spectrum.

### B. Absolute radiation lifetimes

In Table II, we give the absolute radiative lifetimes, calculated by means of Eq. (2), together with the experimental<sup>4</sup> values. The results are compared in a graphical way in Fig. 3. The agreement between experiment and calculation is quite satisfactory. A more detailed analysis shows that some remarks have to be made. Shibuya *et al.*<sup>2</sup> measured  $\tau_r(4^0)$  relative to  $\tau_r(4^1)$ , using the experimental intensity distributions shown in Figs. 1 and 2. They justified their procedure by making two assumptions: first, that all the observed emission bands are progressions of  $2_m^0$  built on  $\Delta\nu_4 = \text{odd}$ ; and second, that the fraction of the band intensities at wavelengths longer than 460 nm is either negligible or the same for the  $4^0$  and  $4^1$  levels. We will show that these assumptions are questionable.

The calculated absolute radiative lifetimes from Table II are obtained by taking into account in Eq. (2) all contributing transitions, including the many bands

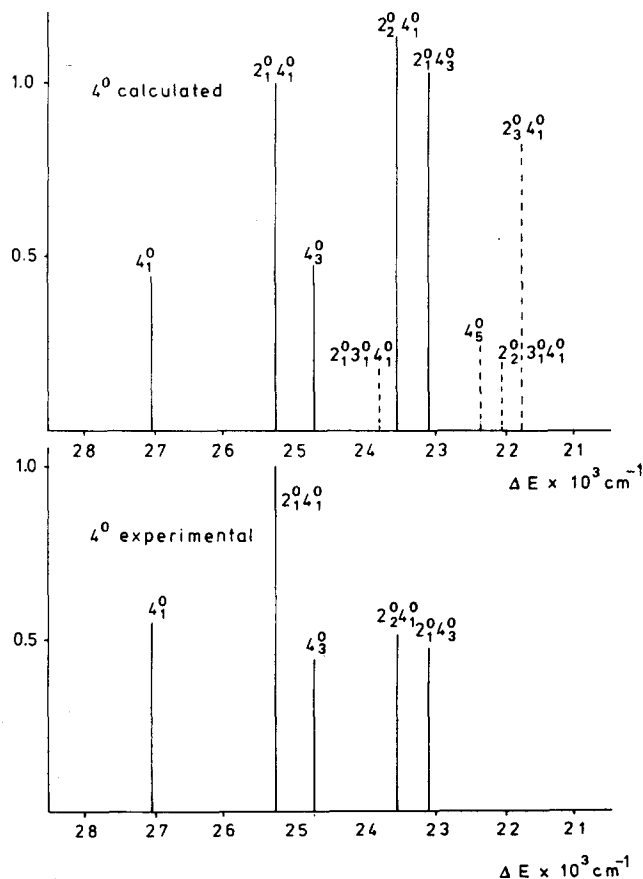


FIG. 2. Calculated and experimental<sup>2</sup> fluorescence emission spectra from the  $4^0$  level. The intensities are relative to the  $2_1^0 4_1^0$  transition. The broken lines are the highest calculated intensities, which are experimentally not found.

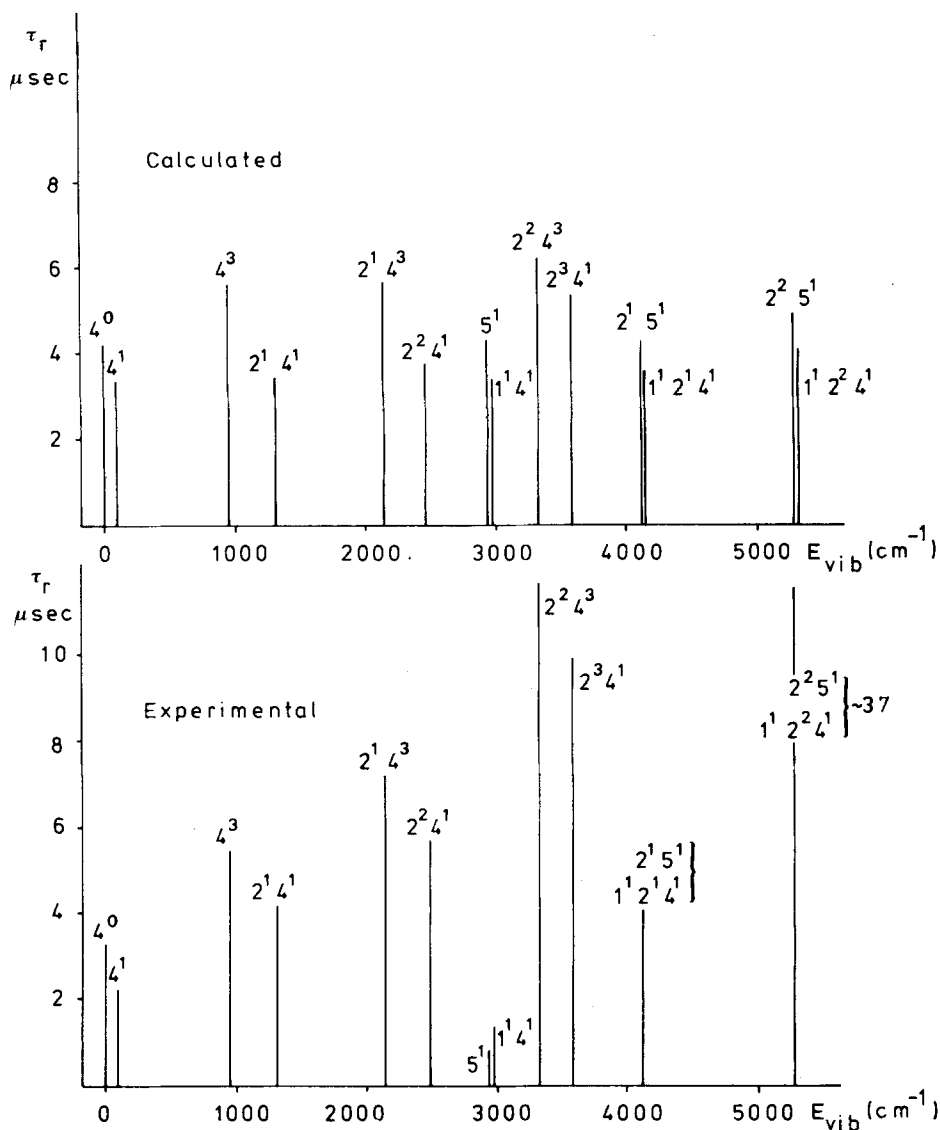


FIG. 3. Calculated and experimental<sup>4</sup> absolute radiative lifetimes of SVL of H<sub>2</sub>CO(<sup>1</sup>A<sub>2</sub>).

with a relatively low oscillator strength (see Table I), and also transitions lying outside the experimental energy region (e. g.,  $2^0$  progressions built on  $4^1$ ,  $4^1_8$ ,  $4^0_3$ ,  $4^0_5$ , etc.). If we only take into account in Eq. (2) the calculated D and  $\Delta E$  values for those bands, which have been used by Shibuya *et al.* in their experimental determination of  $\tau_r(4^1)/\tau_r(4^0)$ , we get  $\tau_r(4^1) = 10.3 \mu\text{sec}$  and  $\tau_r(4^0) = 15.3 \mu\text{sec}$ . The ratio of these values is 0.67, in excellent agreement with Shibuya's experimental value of  $0.68 \pm 0.12$ . It is seen, however, by comparing these  $\tau_r$  values with the ones given in Table II, that the used experimental bands are just responsible for no more than 33% (respectively, 28%) of the total emission intensity of the  $4^1$  (respectively,  $4^0$ ) level. If we include all contributing transitions in the experimental spectral region, i. e., the ones given in Table I, we obtain  $\tau_r(4^1)/\tau_r(4^0) = 8.5 \mu\text{sec}/10.6 \mu\text{sec} = 0.80$ . Only if we also take into account, in Eq. (2), the transitions for wavelengths larger than 460 nm do we arrive at the correct lifetimes given in Table II, with  $\tau_r(4^1)/\tau_r(4^0) = 0.81$ . We find that these long wavelength transitions represent 60% of the total emission intensity.

TABLE II. Calculated and experimental absolute radiative lifetimes of SVL of H<sub>2</sub>CO(<sup>1</sup>A<sub>2</sub>).

SVL	$E_{\text{vib}}$ (cm <sup>-1</sup> )	$\tau_r$ (calc) μsec	$\tau_r$ (exptl) <sup>a</sup> μsec
$4^0$	0	4.2	3.3 <sup>b</sup>
$4^1$	124	3.4	2.3
$4^3$	948	5.5	5.5
$2^1 4^1$	1307	3.4	4.2
$2^1 4^3$	2152	5.6	7.2
$2^2 4^1$	2471	3.7	5.8
$5^1$	2968	4.2	0.8 <sup>c</sup>
$1^1 4^1$	2971	3.4	1.4 <sup>d</sup>
$2^2 4^3$	3343	6.2	11.6
$2^3 4^1$	3621	5.3	~10
$2^1 5^1$	4147	4.4	} 5.1
$1^1 2^1 4^1$	4150	3.5	
$2^2 5^1$	5315	4.9	} ~37
$1^1 2^2 4^1$	5318	4.0	

<sup>a</sup>Experimental values taken from Ref. 4.

<sup>b</sup>Measured relative to  $4^1$ ; see text.

<sup>c</sup>Taken from Ref. 6.

<sup>d</sup>Taken from Ref. 7.

The conclusion from this calculation is that the dependence of the result of a measurement of the emission intensity relative to a reference emission intensity, upon both the sensitivity of the apparatus and the spectral region which is viewed, can be quite large. The sensitivity determines to what extent the large number of low intensity bands are taken into account, while the spectral region has to be quite large to be sure that all the emissions are detected. In experiments where the measurement takes place relative to another compound instead of another vibronic level of the same molecule, these difficulties might cause even larger discrepancies than demonstrated above for the formaldehyde  $4^1$  and  $4^0$  levels. This is because the emission spectrum of the standard compound will, in general, differ more from the emission spectra of the investigated molecule than the mutual differences in the emission spectra of SVL in the same molecule. In their determination of the  $\tau$ , values of formaldehyde, Miller and Lee<sup>4</sup> mention that "In some cases longer wavelength cutoff filters were used for viewing the emission." They conclude from the results (identical fluorescence excitation spectra) that an equal fraction

of the emission is detected for each SVL of formaldehyde. A more quantitative and systematic study concerning this problem, including the fraction of emission of the reference compound (acetone), would be very interesting.

<sup>1</sup>J. M. F. van Dijk, M. J. H. Kemper, J. H. M. Kerp, and H. M. Buck, *J. Chem. Phys.* **69**, 2453 (1978).

<sup>2</sup>K. Shibuya, R. A. Harger, and E. K. C. Lee, *J. Chem. Phys.* **69**, 751 (1978).

<sup>3</sup>J. M. F. van Dijk, Ph.D. thesis, Eindhoven University of Technology, 1977.

<sup>4</sup>R. G. Miller and E. K. C. Lee, *J. Chem. Phys.* **68**, 4448 (1978).

<sup>5</sup>The hot bands given in Ref. 1 are the ones which can be expected for an absorption experiment under normal conditions, i. e., transitions  $X_b^a$  with  $b=0, 1, 2$  for mode 4 and  $b=0, 1$  for the other modes; in fluorescence emission experiments of course many more bands will occur.

<sup>6</sup>R. G. Miller and E. K. C. Lee, *Chem. Phys. Lett.* **33**, 104 (1975).

<sup>7</sup>K. Y. Tang and E. K. C. Lee, *Chem. Phys. Lett.* **43**, 232 (1976).