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Ab initio CI calculation of the vibrational structure of the ${}^1(n\pi^*)$ transition in formaldehyde

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This paper reports an *ab initio* CI calculation of the radiative ${}^1A_1 \rightarrow {}^1A_2$ transition of H_2CO and D_2CO . Throughout the calculation the electronic wavefunctions and transition moments are explicitly calculated as functions of the nuclear geometry, contrary to the conventional Herzberg-Teller approach. The evaluation of the vibrational wavefunctions and integrals was made numerically. The results show that the excited state frequency for mode 3 has to be reassigned and that the calculated vibrational structure agrees well with the experimental intensities.

I. INTRODUCTION

Experimentally the uv spectrum of the ${}^1A_1 \rightarrow {}^1A_2$ transition in formaldehyde is accurately known. Although many *ab initio* calculations have been performed on formaldehyde, no one has yet calculated on an *ab initio* level the detailed ${}^1A_1 \rightarrow {}^1A_2$ uv spectrum of this molecule, for which, apart from the electronic wavefunction and properties, the vibrational wave function and properties also have to be calculated. A description of such a calculation is made in this paper. Much of what follows has also been used in the calculation of the nonradiative decay of formaldehyde (1A_2), as is described in a companion paper.¹

II. METHOD OF CALCULATION

A. Electronic wave function

In order to avoid calculating the six-dimensional potential energy surface and transition dipole moment surface, we approximate these surfaces by calculating along six sections determined by the normal coordinates. The consequences of this procedure will be discussed below.

The atomic orbital basis set used for the calculation of the electronic wave functions of formaldehyde is a contracted Gaussian basis set of double zeta quality given by Dunning²: for carbon and oxygen a $(9s5p)[4s3p]$ set, for hydrogen a $(4s)[2s]$ set. For the present purpose it is necessary to use one MO set to calculate both the ground and excited state. The reason is that transition properties are calculated between the two states. If two different MO sets are used, then rather time-consuming manipulations must be performed to calculate the transition properties. In order to describe ground and excited state with the same accuracy with one MO set, we have to obtain an MO set that is in some way intermediate between those of ground and excited state. One way of doing this is to use the transition orbital method (TOM) developed by Goscinski *et al.*³⁻⁹ This method is especially suited for single excitations, i.e., excitations in which one electron is promoted from MO i to MO a . The HF operator is then changed in such a way that effectively one half electron is removed from the MO i and one half is put into MO a . We work with the

RHF method in which we then have 1.5 electrons in i and 0.5 electron in a . Also, because of the RHF method we have 0.75 α electron and 0.75 β electron in i , and 0.25 α and 0.25 β electron in a . To select the configurations for the CI calculation we use the point system of Morokuma.^{10,11} The points assigned to each MO are taken from Ref. 11. We included 175 configurations in the CI calculation. The calculations were performed with the IBMOL5, H package.¹² The SCF part was modified to allow the calculation of TOM MO's.

B. Transition dipole moment

The electric dipole transition moment is calculated in two ways,

$$\text{dipole length } {}^L D_{10}(Q) = \langle \phi_1(q, Q) | \sum_i q_i | \phi_0(q, Q) \rangle_q, \quad (\text{II. 1})$$

dipole acceleration ${}^A D_{10}(Q)$

$$= [\Phi_0(Q) - \Phi_1(Q)]^{-2} \cdot \langle \phi_1(q, Q) | \sum_i \nabla_i V | \phi_0(q, Q) \rangle_q, \quad (\text{II. 2})$$

with q and Q the complete set of electron and nuclear coordinates, respectively, q_i the x, y , and z coordinates of electron i ,⁷ $\nabla_i = \partial/\partial q_i$, $\phi_0(q, Q)$ and $\phi_1(q, Q)$ the adiabatic Born-Oppenheimer functions for electronic ground and excited states, respectively. $\Phi_0(Q)$ and $\Phi_1(Q)$ are the eigenvalues of $\phi_0(q, Q)$ and $\phi_1(q, Q)$, respectively. V is the potential energy part of the Hamiltonian. The subscript q denotes an integration over the electron coordinates; the result is a function of the nuclear coordinates Q .

The dipole transition moments were calculated with the POLYATOM property package,¹² which was modified to allow the calculation of properties between different CI functions. The integrals occurring in ${}^A D(Q)$ are integrals over the electric field operator.¹³

The total dipole transition moment between two vibronic states is obtained by integrating $D(Q)$ between these states

$$D = \langle \chi_{1p}(Q) | D(Q) | \chi_{0q}(Q) \rangle_Q \quad (\text{II. 3})$$

with $\chi_{0q}(Q)$ the q th vibrational wave function for the electronic ground state and $\chi_{1p}(Q)$ the p th vibrational wave function for the electronic excited state.

To simplify the calculation we assume that $D(Q)$ can be written as

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$$D(Q) = D(Q_0) + \sum_k D(Q_k), \quad (\text{II. 4})$$

in which Q_0 is the ground state equilibrium geometry, and Q_k are the normal coordinates for the ground state.

The reason is that with (II. 4) we only need to calculate $D(Q)$ for six sections of the potential energy surface. The effect of assumption (II. 4) is that transitions induced by correction terms to (II. 4) will not be calculated, however, these transitions turn out to form only a minor part of the spectrum (see also Sec. III).

We assume concerning the potential energy surface that

$$\Phi_i(Q) = \Phi_i(Q_0) + \sum_k \Phi_i(Q_k). \quad (\text{II. 5})$$

Then we can write

$$\chi_{1n}(Q) = \prod_k \chi_{1n}(Q_k) \quad (\text{II. 6})$$

in which $\chi_{1n}(Q_k)$ is the vibrational wave function for coordinate Q_k . This is *not* the harmonic approximation, because $\Phi_i(Q_k)$ is calculated with the *ab initio* CI program, and will in general not be a quadratic function. The reason for the assumption of (II. 5) is the same as used for (II. 4), and also that we can only calculate one-dimensional vibrational eigenfunctions. The effect of (II. 5) is that intermode coupling in one electronic state is neglected. The validity of (II. 5) can be checked by comparing the calculated and experimental frequencies (see Sec. III). It is observed from (II. 5) that we take the same normal coordinates for both ground and excited state, i. e., we neglect the so-called Duschinsky effect.¹⁴

From the equations (II. 3), (II. 4), and (II. 6) we obtain

$$D = D(Q_0) \cdot \prod_n \langle \chi_{1p}(Q_n) | \chi_{0q}(Q_n) \rangle_{Q_n} + \sum_k \prod_{n \neq k} \langle \chi_{1p}(Q_k) | D(Q_k) | \chi_{0q}(Q_k) \rangle_{Q_k} \cdot \langle \chi_{1p}(Q_n) | \chi_{0q}(Q_n) \rangle_{Q_n}. \quad (\text{II. 7})$$

We now have only one-dimensional vibrational wave functions and integrals.

The normal coordinates were determined by using the ten force constants determined by Duncan and Mallison¹⁵ for the general harmonic force field. These force constants were used in the Schachtschneider programs,¹⁶ to determine the normal coordinates. We assume that the normal coordinates of the D_2CO molecule are equal to those of H_2CO , except for a constant depending on the mode considered. The following relations hold

$$\left. \begin{aligned} V &= \frac{1}{2} \omega^2 \cdot Q^2 \\ V &= \frac{1}{2} (\omega^t)^2 \cdot (Q^t)^2 \end{aligned} \right\} Q^t = \frac{\omega}{\omega^t} Q. \quad (\text{II. 8})$$

The *i* superscripted quantities are for D_2CO and the others for H_2CO ; ω/ω^t is determined from experiment.¹⁵ It should be noted that these experimental values are only used for the determination of the normal coordinates of D_2CO . The calculated and experimental ω/ω^t are not automatically the same by this procedure however; this is only the case if the calculated potential energy curves are quadratic functions. The HDCO molecule is not considered here, because the different symmetry makes a comparison with H_2CO and D_2CO impossible.

C. Vibrational wave function

The vibrational eigenfunctions and eigenvalues are determined by integrating the differential equations for the vibrational functions numerically with the integration procedure from the TRAPRB program written by W. R. Jarman and J. C. McCallum.¹⁷⁻¹⁹ In this way the vibrational eigenfunctions and eigenvalues for an arbitrary numerical energy function can be determined. The potential energy occurring in the vibrational equation was obtained from the *ab initio* CI calculation. The number of integration points is 200–800/Å, depending on the number of nodes the wave function contains. The potential energy curve is calculated in all these points by fitting cubic splines to the points calculated with the *ab initio* CI program. The vibrational integrals necessary for the evaluation of the dipole transition moment [see (II. 7)] are also evaluated numerically.

III. RESULTS AND COMPARISON WITH EXPERIMENT

The energies of the ground and ${}^1(\nu_2\pi^*)$ excited state of formaldehyde were calculated as a function of the six normal coordinates. About 14 points per normal coordinate were calculated. Also were calculated for each point the three Cartesian components of the dipole transition moments 2D and 4D . See Fig. 1 for the potential energy curves. The point 0 on the horizontal axis in the figures is the point Q_0 of Eq. (II. 4). The experimental equilibrium point, used for the normal coordinate calculation of the ground state, was taken for the point Q_0 .¹⁵ The point 0 on the vertical axis corresponds to -113.8619888 a. u. The calculated equilibrium values for the 1A_1 and 1A_2 states for each of the internal coordinates are obtained from Fig. 1. They are compared with the experimental ones²⁰ in Table I. (θ is the out-of-plane angle.)

TABLE I. The calculated equilibrium geometries.

	1A_1		1A_2	
	Experimental	Calculated	Experimental	Calculated
θ deg.	0.0	0.0	33.6	30
HCH deg.	116.52	116.5	118.0	112.5
C–H Å	1.1161	1.10	1.0947	1.06
C–O Å	1.2078	1.23	1.3252	1.36

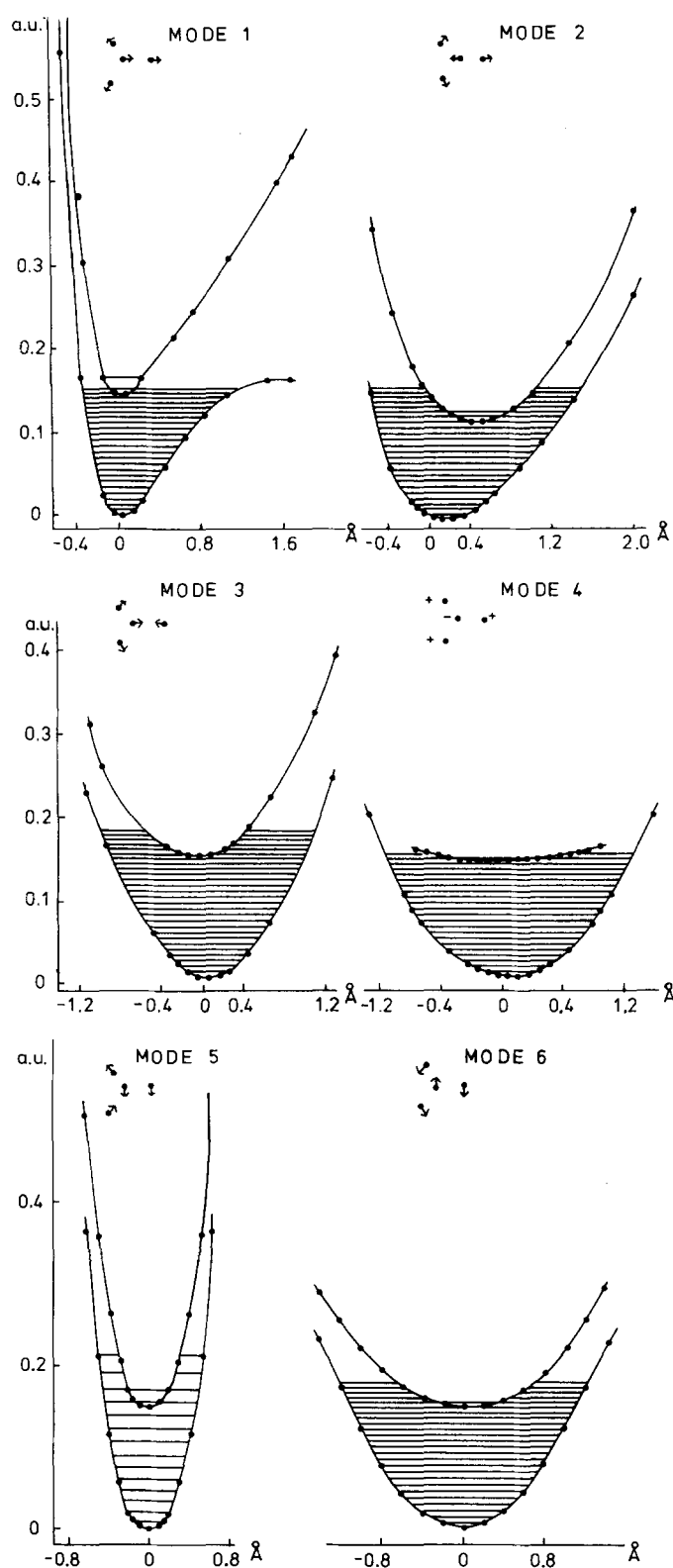


FIG. 1. Calculated potential energy curves for ground and excited state. The different modes and vibrational levels are indicated schematically.

The dipole length moment in Q_0 for ground and excited state is shown in Table II. To be completely comparable with experiment, one has to calculate the dipole moment for the zero vibrational state, which will lower the calculated value somewhat.

TABLE II. The dipole length moments.

	Dipole moment (a.u.)	
	Calculated ^a	Experimental
1A_1	-1.114	-0.920 ^b
1A_2	-0.652	-0.614 ^c

^aCalculated in Q_0 . ^cFrom Ref. 22.

^bFrom Ref. 21.

Concerning the calculation of the potential energy curves for mode 4 the following can be remarked. We first used the linear normal coordinate for the out of plane movement. For the 1A_2 state this resulted in an energy lowering of 25 cm^{-1} (with as reference energy the energy in the point Q_0) for an out-of-plane angle of 30°. Next we used the nonlinear out-of-plane coordinate, that leaves the bond lengths intact. Using this coordinate resulted in an energy depression of 157 cm^{-1} , again at 30°. The experimental energy dip (from the frequencies of the vibrational progression in mode 4 of the excited state) is 356 cm^{-1} . The reason for this discrepancy is discussed in Sec. IV. We therefore used for the excited state potential of mode 4 the experimentally determined energy curve^{21,23} to determine the vibrational eigenfunctions which are used in order to calculate overlap integrals and integrals over the transition dipole moment. The agreement between the obtained eigenvalues and the experimental frequencies (see Table III), shows the numerical stability of the programs used. The ground state energy curve and the transition dipole elements were calculated with the electronic wavefunc-

TABLE III. Calculated and experimental ir transitions (cm^{-1}).

Mode	H_2CO		D_2CO	
	Exp. ^a	Calcul.	Exp. ^a	Calcul.
1A_1 state				
1(0-1) ^d	2766.4	2796.2	2055.8	2041.6
2(0-1)	1746.1	1651.0	1700	1612.3
3(0-1)	1500.6	1546.3	1105.7	1117.2
4(0-1)	1167.3	1242.3	933.8	1004.1
5(0-1)	2843.4	2656.0	2159.7	1974.8
6(0-1)	1251.2	1325.5	990.4	1049.8
1A_2 state				
1(0-1) ^d	2847	3157.7	2079	2348.9
2(0-1)	1173	1345.0	1176	1309.8
3(0-1)	887	1495.9	(625) ^e	1107.2
	(1429) ^b		(1009) ^b	
4(0-1)	124.6	125.9 ^c	68.5	67.8 ^c
4(1-2)	417.7	419.4 ^c	318.5	327.4 ^c
4(2-3)	405.6	408.5 ^c	281.0	286.5 ^c
5(0-1)	2968	2767.2	2233	2070.4
6(0-1)	904	988	705	781.3

^aExperimental data from Ref. 23.

^bRevised assignment, see text.

^cCalculated from the experimental potential, see text.

^dIn this table 1(0-1) means the $\nu=0 \rightarrow \nu=1$ transition in mode 1, etc.

^eNot observed, but calculated from Teller-Redlich product rule ratios by Job *et al.*²³

tions obtained for the linear normal coordinate path. The calculated 0-0 transition energy for H_2CO is $24\,757\text{ cm}^{-1}$. The experimental 0-0 transition lies at $28\,188\text{ cm}^{-1}$. So there is an underestimation of $3\,431\text{ cm}^{-1}$, which is of the order of magnitude for the error in a calculation of this type.^{24,25} This error is due to the omission of polarization functions, the relatively small CI and errors in calculating the zero-vibrational energy levels; the exact influence of these factors is very difficult to establish. The calculated difference between the H_2CO and D_2CO 0-0 transition is -453 cm^{-1} ; experimentally it is -113 cm^{-1} .²³

The calculated vibrational frequencies for the lowest ir transitions in ground and excited state for H_2CO and D_2CO are listed in Table III, where they are compared with the experimental data.

It appears that, apart from mode 3 in the excited state, the calculation can reproduce the experimental results to within $30\text{--}300\text{ cm}^{-1}$; the largest discrepancy occurs for the excited state mode 1.

Mode 3 of the excited state is particularly intriguing. Experimentally the assignment of ν_3 is rather problematic.²³ It is in fact based on only two bands: the first one a type *B* band in HDCO at 874 cm^{-1} from the 0-0 band. This 874 cm^{-1} band is assigned by Job *et al.*²³ to $3_0^1 4_0^1$; however, this band does not occur in H_2CO and D_2CO spectra at the required places. The other one is a type *B* hot band in H_2CO at 262 cm^{-1} from the 0-0 band. The latter band is assigned by Job *et al.*²³ to $3_0^1 4_1^2$, resulting in a $\nu_3 = 887\text{ cm}^{-1}$. We calculate, however, that the $3_0^1 4_1^0$ band has an intensity 17 times larger than the $3_0^1 4_1^2$ band (see Table VI); assigning $3_0^1 4_1^0$ to this band re-

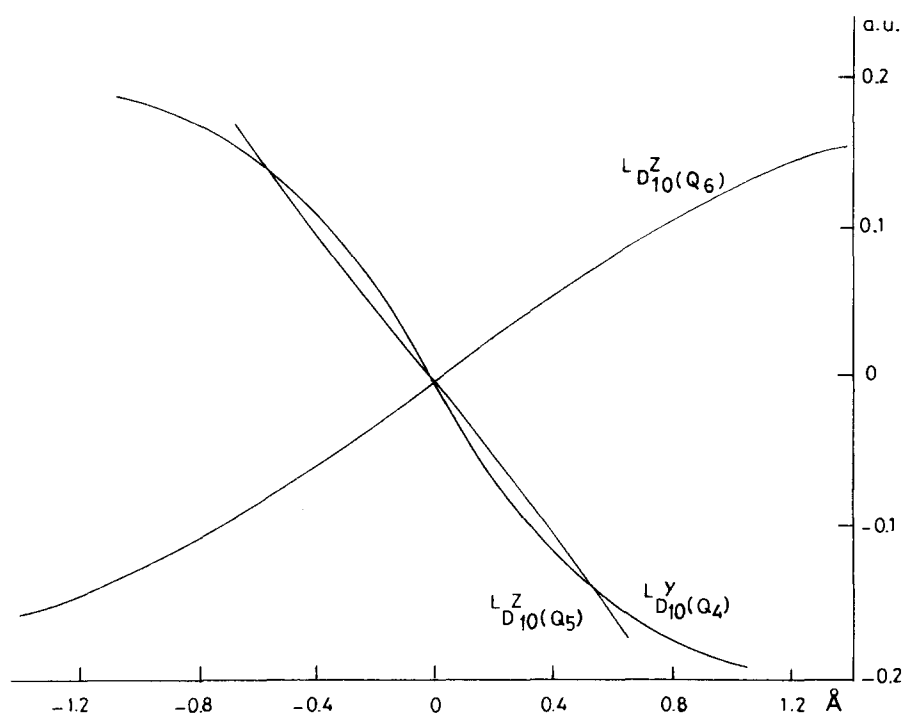
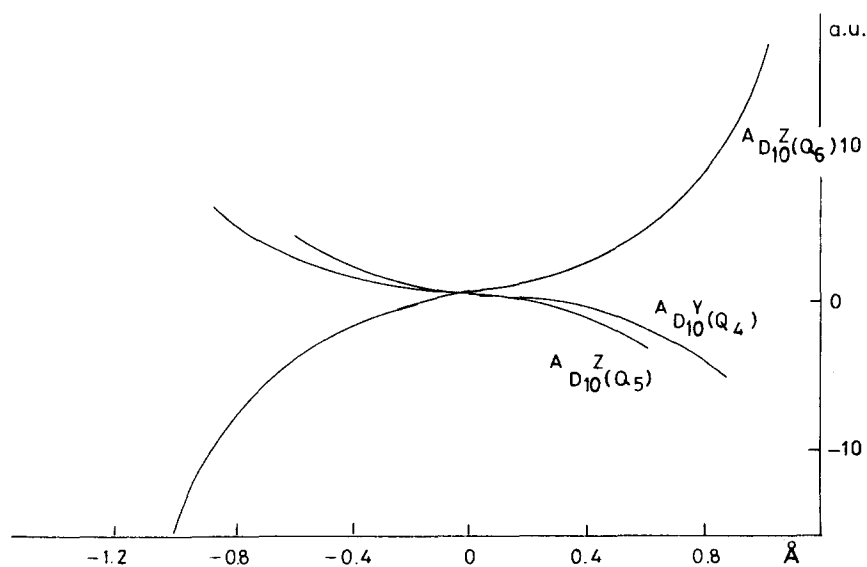


FIG. 2. The nonzero components of the dipole length, $L_{D_{10}}^Z(Q)$, and dipole acceleration, $A_{D_{10}}^Z(Q)$, electronic transition moments in dependence on the normal coordinates.



sults in a $\nu_3=1429\text{ cm}^{-1}$, which is in the expected range from the calculated value of 1495.9 cm^{-1} . Applying Teller-Redlich product rule ratios with the revised assignment one obtains for ν_3 in D_2CO 1009 cm^{-1} and in HDCO 1290 cm^{-1} . Sethuraman *et al.*²⁸ have deduced from the rotational fine structure that the band in H_2CO , 262 cm^{-1} from the 0-0 band, has a type C Coriolis interaction with the $4^2_6 1$ level that lies 17 cm^{-1} above it. This finding is also compatible with the $3_0^1 4_1^0$ assignment of the 262 cm^{-1} band.

Formaldehyde is an asymmetric top molecule. Therefore there are three types of bands in the $^1A_1 \rightarrow ^1A_2$ spectrum: type A, B, and C bands. In formaldehyde the type A bands have an intensity of 3-5% of the type B bands.²³ It is estimated from experiment that the type B bands contribute 75% of the total oscillator strength, the rest being type C. From symmetry considerations²⁷ one can derive that mode 4 should give a transition moment along the y axis (type B bands), and mode 5 and 6 along the z axis (type C bands), all other transition moments being zero. (The axes are defined in such a way that the carbon atom is the origin; the CO-bond lies on the x axis and the planar molecule defines the xy plane.) This is also what we find with our calculations; The resulting three transition dipole length and acceleration moments are shown in Fig. 2.

It is observed in this figure that the acceleration dipole transition moments are 3-80 times larger than the corresponding length moments. This is a fact well known in the very few calculations that have so far been done with the acceleration formula.²⁸⁻³¹ It turns out that the acceleration formula depends very sensitively upon the wave function close to the nuclei, because of the $1/r^2$ term in the operator.³² The dipole length form of the transition moment depends more strongly on the wave function farther from the nuclei; therefore,

the dipole length form is always more accurate than the acceleration form,²⁸⁻³¹ because the wave functions are obtained by applying the variation principle on the energy operator, which only has a $1/r$ dependence.

So comparing the acceleration and length moments gives an estimate of the accuracy of the electric field transition components. From this comparison one estimates that these electric field transition moments are probably a factor 3 to 80 too large. The electric field components for the ground state of formaldehyde have been calculated by Neumann and Moskowitz³³ with a HF function using a basis set of double zeta plus polarization functions. Our calculations give results for these electric field components which differ at most 15% from their calculation.

In Tables IV and V overlap integrals and transition dipole length integrals are listed. With formula (II. 7) we can calculate the oscillator strength from it. We present the complete Tables IV and V because from the integrals we can predict which bands will and which will not occur in the spectrum; the oscillator strengths of the allowed bands are shown in Table VI. With Table IV we can predict which "cold" (starting from χ_{00}) bands will occur in the uv spectrum of formaldehyde. First we have to remark that we are here only considering bands with type B or C polarization, as the type A bands are magnetic dipole transitions²³ or transitions caused by a combination of odd quanta in the B_1 (mode 4) and B_2 (mode 5 and 6) vibrations.²³ The latter combination transitions are not found with the present treatment, because it was assumed that the six-dimensional integral for the transition moment can be approximated by a product of six one-dimensional integrals [see Eq. (II. 5)]. To calculate the combination bands with A polarization, one would have to retain the two-dimensional integral over coordinates 4 and 5, or 4 and 6. From Table IV

TABLE IV. Integrals^a of H_2CO and D_2CO for the cold bands.

Mode	Integral ^b	Molecule	k						
			0	1	2	3	4	5	6
1	001k	H_2CO	0.98	0.17	0.37(-1)	0.26(-3)	-0.13(-2)	0.16(-2)	-0.31(-3)
	001k	D_2CO	0.98	0.20	0.46(-1)	0.25(-2)	-0.18(-2)	0.11(-2)	0.59(-3)
2	001k	H_2CO	0.31	-0.44	0.48	-0.45	0.37	-0.28	0.19
	001k	D_2CO	0.30	-0.44	0.48	-0.45	0.38	-0.28	0.20
3	001k	H_2CO	0.91	0.40	0.11	0.22(-1)	-0.32(-3)	-0.59(-2)	-0.39(-2)
	001k	D_2CO	0.88	0.45	0.16	0.43(-1)	0.60(-2)	-0.59(-2)	-0.58(-2)
4	001k	H_2CO	0.71	0.20(-4)	-0.64	0.64(-5)	0.28	-0.82(-5)	-0.11
	001k	D_2CO	0.62	0.71(-5)	-0.70	0.30(-5)	0.33	-0.19(-5)	-0.14
	00D1k	H_2CO	-0.20(-5)	-0.23(-1)	-0.20(-5)	-0.25(-1)	0.18(-6)	-0.15(-1)	0.14(-5)
	00D1k	D_2CO	-0.73(-6)	-0.19(-1)	-0.69(-6)	0.22(-1)	-0.76(-7)	-0.15(-1)	0.38(-6)
5	001k	H_2CO	1.0	0.49(-8)	0.93(-2)	-0.19(-8)	-0.52(-3)	0.13(-8)	-0.46(-3)
	001k	D_2CO	1.0	0.47(-7)	0.10(-1)	-0.51(-10)	0.68(-4)	0.14(-10)	-0.56(-3)
	00D1k	H_2CO	-0.12(-9)	-0.21(-1)	-0.11(-8)	-0.42(-3)	0.20(-10)	-0.11(-4)	-0.95(-11)
	00D1k	D_2CO	-0.13(-9)	-0.19(-1)	-0.13(-8)	-0.39(-3)	0.14(-11)	-0.16(-4)	-0.41(-12)
6	001k	H_2CO	0.99	0.36(-6)	-0.10	0.60(-10)	0.12(-1)	0.35(-8)	-0.15(-2)
	001k	D_2CO	0.99	0.20(-6)	-0.82(-8)	-0.19(-7)	0.13(-1)	0.55(-8)	-0.16(-2)
	00D1k	H_2CO	-0.59(-11)	0.16(-1)	0.73(-11)	0.28(-2)	-0.91(-12)	0.44(-3)	0.59(-11)
	00D1k	D_2CO	0.31(-9)	0.14(-1)	-0.25(-2)	-0.25(-2)	-0.74(-10)	0.40(-3)	0.41(-10)

^a(-6) means 10^{-6} .

^b00D1k = $\langle \chi_{00} | \sum_i \mathbf{D} | \chi_{1k} \rangle$.

TABLE V. Integrals^a of H₂CO for the hot bands.

Mode H ₂ CO	Inte- gral ^b	<i>k</i>							
		0	1	2	3	4	5	6	
1	0 <i>k</i> 10	0.98	-0.17	0.59(-2)	0.77(-2)	-0.23(-2)	-0.12(-2)	0.14(-2)	
	0 <i>k</i> 11	0.17	0.96	-0.23	0.21(-1)	0.75(-2)	-0.43(-2)	0.35(-4)	
2	0 <i>k</i> 10	0.31	0.48	0.53	0.47	0.34	0.21	0.12	
	0 <i>k</i> 11	-0.44	-0.41	-0.12	0.22	0.42	0.44	0.35	
	0 <i>k</i> 12	0.48	0.16	-0.26	-0.36	-0.13	0.19	0.38	
3	0 <i>k</i> 13	-0.45	0.11	0.35	0.66(-1)	-0.28	-0.31	-0.62(-1)	
	0 <i>k</i> 10	0.91	-0.39	0.12	-0.32(-1)	0.84(-2)	0.85(-3)	-0.25(-2)	
4	0 <i>k</i> 10	0.71	0.87(-4)	0.53	0.73(-3)	0.39	-0.95(-3)	0.22	
	0 <i>kD</i> 10	-0.20(-5)	-0.54(-1)	-0.40(-4)	-0.58(-1)	-0.11(-3)	-0.44(-1)	0.31(-3)	
	0 <i>k</i> 11	0.20(-4)	0.62	0.39(-3)	0.59	1.00(-3)	0.43	-0.30(-2)	
	0 <i>kD</i> 11	-0.23(-1)	-0.15(-4)	-0.67(-1)	-0.15(-3)	-0.71(-1)	0.13(-3)	-0.47(-1)	
	0 <i>k</i> 12	0.64	0.10(-3)	0.23	0.13(-2)	0.50	-0.32(-3)	0.42	
	0 <i>kD</i> 12	0.20(-5)	0.13(-1)	-0.52(-4)	-0.47(-1)	-0.26(-3)	-0.68(-1)	0.43(-3)	
	0 <i>k</i> 13	0.64(-5)	-0.64	0.29(-3)	0.67(-1)	0.32(-2)	0.45	-0.26(-2)	
	0 <i>kD</i> 13	0.25(-1)	-0.63(-5)	0.32(-1)	-0.14(-3)	-0.36(-1)	-0.17(-3)	-0.69(-1)	
5	0 <i>k</i> 10	1.0	0.41(-7)	-0.93(-2)	0.13(-7)	0.61(-3)	0.28(-9)	0.42(-3)	
	0 <i>kD</i> 10	-0.12(-9)	-0.21(-1)	-0.11(-8)	0.13(-3)	0.46(-11)	-0.10(-3)	-0.19(-11)	
	0 <i>k</i> 11	0.48(-8)	1.0	0.53(-7)	-0.12(-1)	0.23(-11)	0.25(-2)	-0.38(-10)	
	0 <i>kD</i> 11	-0.21(-1)	-0.22(-9)	-0.28(-1)	-0.53(-8)	-0.39(-4)	-0.88(-11)	-0.19(-3)	
6	0 <i>k</i> 10	0.99	0.69(-7)	0.10	0.60(-7)	0.13(-1)	0.65(-10)	0.16(-2)	
	0 <i>kD</i> 10	-0.59(-11)	0.18(-1)	0.60(-11)	0.32(-2)	0.15(-11)	0.48(-3)	0.41(-11)	
	0 <i>k</i> 11	0.36(-9)	0.98	-0.20(-6)	0.17	0.75(-7)	0.27(-1)	-0.28(-7)	
	0 <i>kD</i> 11	0.16(-1)	0.13(-8)	0.27(-1)	0.55(-8)	0.63(-2)	0.16(-8)	0.11(-2)	

^a(-6) means 10⁻⁶.^b0*kD*10 = ⟨χ_{0*k*}^LD | χ₁₀⟩.

we can derive which changes in the vibrational quantum number of each mode can occur as part of an observable S₀ → S₁ transition. From Table IV we get the cold transitions. As a criterion we take that the individual integral has to be larger than 0.16. This is admittedly a somewhat arbitrary number as it depends on the experimental expertise, which transition is still observable, and which not. We get (the indicated polarization is the possible polarization of the "total" transition):

1 ⁰ and 1 ¹	(B or C polarization)
2 ⁰ , 2 ¹ , 2 ² , 2 ³ , 2 ⁴ , 2 ⁵ , and 2 ⁶	(B or C polarization)
3 ⁰ and 3 ¹	(B or C polarization)
4 ¹ , 4 ³ , and 4 ⁵	(B polarization)
4 ⁰ and 4 ²	(C polarization)
5 ⁰	(B polarization)
5 ¹	(C polarization)
6 ⁰	(B or C polarization)
6 ¹	(C polarization)

All these are found in the spectra^{23,34}; there are no experimentally found transitions with B or C polarization that are not found with the calculation. All calculated polarizations agree with the experimental ones. The hot bands in H₂CO are obtained from Table V:

1 ^{0*} and 1 ^{1*}	(B or C polarization)
2 ^{0*} and 2 ^{1*}	(B or C polarization)
3 ^{0*}	(B or C polarization)

4 ⁰	(B polarization)
4 ^{1*} and 4 ^{3*}	(C polarization)
4 ² and 4 ^{5*}	(B polarization)
4 ^{0*}	(C polarization)
5 ^{0*}	(C polarization)
6 ⁰	(C polarization)

The asterisk marked ones are experimentally not found, while the others are found; all polarizations agree with the experimental ones. The hot bands from modes 1 and 5 are not seen experimentally, because the first excited level in these modes has a rather high energy (3000 cm⁻¹). There is one experimental transition that is not found in the calculation, 4². This one occurs in the combination assigned 3¹₀4²₁ at 28 450 cm⁻¹ with B polarization. For the 3¹₀4⁰₁ band the calculated intensity is 17 times that of the 3¹₀4²₁ transition (see Table VI) as was already alluded to before. With the revised value for ν₃ the transition does not occur in H₂CO. From Table IV it can be seen that the integrals for H₂CO and D₂CO differ only slightly. That is why in Table V (for calculation of the hot bands) only the H₂CO values are shown. In the cold experimental spectrum, the same transitions occur for H₂CO and D₂CO. The hot spectrum of D₂CO shows an extra transition when compared with H₂CO: 4². Calculating the oscillator strength of this transition it is found that for D₂CO it is 2.5 times stronger than for H₂CO (see Table VI). This is due to the fact that for this transition all D₂CO integrals are accidentally larger than the corresponding ones for H₂CO; so this is in agreement with the experiment. Also

TABLE VI. Calculated oscillator strengths for experimentally observed transitions.

Number	Transition ^a	ΔE (cm ⁻¹)	$ D ^b$	f^b	Polarization
H ₂ CO Cold					
1	4 ₀ ¹	28312	0.629(-2)	3.41(-6)	B
2	4 ₀ ³	29136	0.684(-2)	4.15(-6)	B
3	2 ₀ ¹ 4 ₀ ¹	29495	0.893(-2)	7.15(-6)	B
4	4 ₀ ² 6 ₀ ¹	29634	0.283(-2)	0.72(-6)	C
5	3 ₀ ¹ 4 ₀ [*]	29742	0.276(-2)	0.69(-6)	B
6	2 ₀ ¹ 4 ₀ ³	30340	0.971(-2)	8.72(-6)	B
7	3 ₀ ¹ 4 ₀ [*]	30565	0.301(-2)	0.84(-6)	B
8	2 ₀ ² 4 ₀ ¹	30659	0.974(-2)	8.85(-6)	B
9	2 ₀ ¹ 4 ₀ ² 6 ₀ ¹	30819	0.402(-2)	1.51(-6)	C
10	2 ₀ ¹ 3 ₀ ¹ 4 ₀ [*]	30914	0.392(-2)	1.45(-6)	B
11	5 ₀ ¹	31156	0.408(-2)	1.58(-6)	C
12	1 ₀ ¹ 4 ₀ ¹	31159	0.109(-2)	0.12(-6)	B
13	2 ₀ ² 4 ₀ ³	31531	1.059(-2)	10.42(-6)	B
14	2 ₀ ¹ 3 ₀ ¹ 4 ₀ [*]	31738	0.427(-2)	1.76(-6)	B
15	2 ₀ ³ 4 ₀ ¹	31809	0.913(-2)	8.07(-6)	B
16	1 ₀ ¹ 4 ₀ ³	31987	0.112(-2)	0.12(-6)	B
17	2 ₀ ¹ 5 ₀ ¹	32335	0.579(-2)	3.30(-6)	C
18	1 ₀ ¹ 2 ₀ ¹ 4 ₀ ¹	32335	0.155(-2)	0.24(-6)	B
19	2 ₀ ³ 4 ₀ ³	32699	0.993(-2)	9.80(-6)	B
20	2 ₀ ⁴ 4 ₀ ¹	32949	0.751(-2)	5.64(-6)	B
21	1 ₀ ¹ 2 ₀ ¹ 4 ₀ ³	33332	0.168(-2)	0.43(-6)	B
22	2 ₀ ² 5 ₀ ¹	33535	0.632(-2)	4.06(-6)	C
23	1 ₀ ¹ 2 ₀ ² 4 ₀ ¹	33535	0.169(-2)	0.29(-6)	B
24	2 ₀ ⁵ 4 ₀ ¹	34083	0.569(-2)	3.35(-6)	B
25	2 ₀ ³ 5 ₀ ¹	34698	0.592(-2)	3.70(-6)	C
26	1 ₀ ¹ 2 ₀ ³ 4 ₀ ¹	34698	0.158(-2)	0.26(-6)	B
27	2 ₀ ⁶ 4 ₀ ¹	35090	0.386(-2)	1.59(-6)	B
28	1 ₀ ¹ 2 ₀ ⁴ 4 ₀ ³	35740	0.142(-2)	0.22(-6)	B
29	2 ₀ ⁶ 4 ₀ ³	36220	0.419(-2)	1.94(-6)	B
30	1 ₀ ¹ 2 ₀ ⁵ 4 ₀ ¹	37250	0.099(-2)	0.11(-6)	B
D ₂ CO Hot					
31	3 ₀ ¹ 4 ₁ ²	28450	0.156(-2)	0.21(-6)	B
32	3 ₀ ¹ 4 ₁ ⁰	28450	0.648(-2)	3.64(-6)	B
33	4 ₁ [*]	27563	0.355(-2)	1.06(-6)	B
34	2 ₀ ¹ 4 ₂ ¹	27241	2.601(-2)	56.12(-6)	B
35	4 ₁ ⁰	27021	1.478(-2)	17.94(-6)	B
36	2 ₀ ¹ 4 ₀ ¹	26567	0.975(-2)	7.61(-6)	B
37	4 ₂ ¹	26061	1.834(-2)	26.63(-6)	B
38	4 ₁ ²	27753	0.561(-2)	2.65(-6)	B

^a* Means not observed in the experimental spectrum.

^b(-6) means 10⁻⁶.

the 4₁ level in D₂CO will be more populated than the corresponding one in H₂CO at the same temperature because the energy of it is lower (see Table III). In Table VI the calculated oscillator strengths are shown for all observed bands in H₂CO and also for the bands involving mode 3, using 1429 cm⁻¹ for ν_3 .

One can see again that it is extremely unlikely that the 3₀¹4₁² hot band can be observed in the spectrum, noting the large oscillator strengths apparently necessary to observe a band in the hot spectrum at all. To illustrate the procedure used we will calculate the oscillator strength for the 2₀¹5₀¹ transition in H₂CO. The following term of the dipole transition moment is not equal to zero [see Eq. (II. 7)]

$$D^z = \langle \chi_{10}(Q_1) | \chi_{00}(Q_1) \rangle \langle \chi_{11}(Q_2) | \chi_{00}(Q_2) \rangle \\ \times \langle \chi_{10}(Q_3) | \chi_{00}(Q_3) \rangle \langle \chi_{10}(Q_4) | \chi_{00}(Q_4) \rangle \\ \times \langle \chi_{11}(Q_5) | D_{10}^z(Q_5) | \chi_{00}(Q_5) \rangle \langle \chi_{10}(Q_6) | \chi_{00}(Q_6) \rangle .$$

It should be noted here that $D(Q_0) = 0$.

Now Table IV furnishes the numbers:

$$D^z = 0.98 \times (-0.44) \times 0.91 \times 0.71 \times (-0.021) \times 0.99 = 0.0058$$

The oscillator strength is given by $f = \frac{2}{3} \Delta E |D|^2$. Substituting for ΔE the experimental energy difference (in a. u.) of this transition, we obtain $f = 3.295 \times 10^{-6}$. As the dipole transition moment of 2₀¹5₀¹ has only a component in the z direction, the polarization in C.

Recently an experimental spectrum has been published, in which the intensities of the different transitions are shown.³⁵ The calculated intensities agree well with the experimental ones. As an illustration we compare in Fig. 3 for the first part of the spectrum the oscillator strengths from Table VI with the experimental peak heights, as far as we could deduce these from Lee's work.³⁵ The agreement for higher energies is difficult to judge, because the spectrum becomes diffuse in that region, due to the large number of bands involved. In view of the uncertainty in our determination of Lee's peak heights, the agreement is quite satisfying. One may note, that the peaks 4, 5, 7, 10, and 14 are not found in Lee's experimental spectrum. This is due to the fact that, according to our calculations all these peaks have very low oscillator strengths, and also because they all lie very close to peaks with high oscillator strength. Peak 4 has however been observed by Job *et al.*,²³ the other ones have never been observed, but they have never been looked for due to the wrong assignment of mode 3.

IV. DISCUSSION

It is seen that it is possible to calculate the uv spectrum of formaldehyde fairly accurately with an *ab initio* CI calculation. For sake of clarity we will briefly recapitulate to what extent use was made of experimental quantities in this calculation:

The normal coordinates are determined from the experimental spectrum. We use the normal coordinates because we want to avoid calculating the whole potential energy surface. If one wants to represent the potential

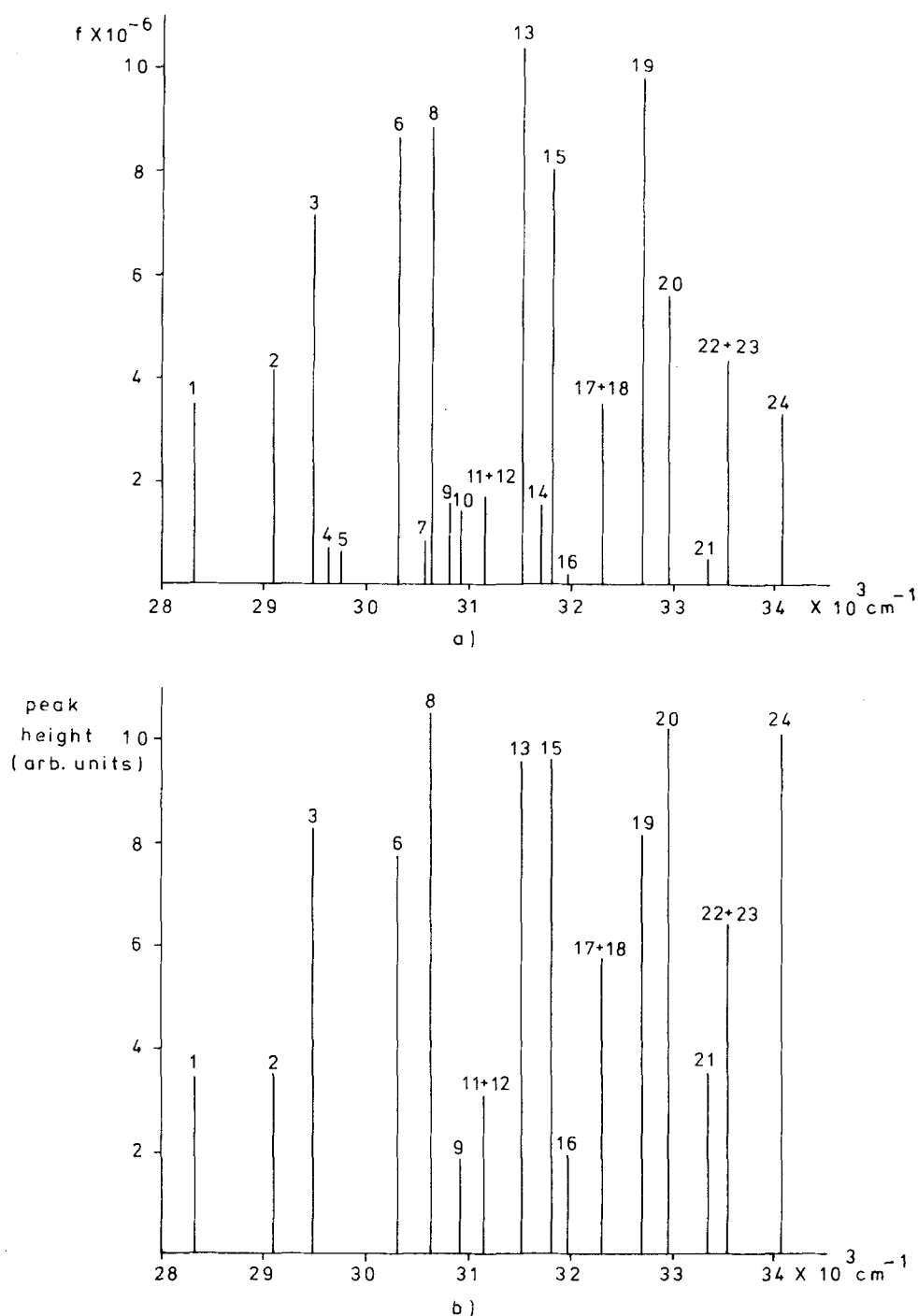


FIG. 3. Calculated (a) and experimental (b) vibrational structure of the cold $1(n\pi^*)$ transition in H_2CO . The experimental peak heights are taken as well as possible from Ref. 35. The numbers correspond with the transitions given in Table VI; the experimental height for transition 1 is adjusted to the calculated value.

energy surface by six sections only, then the ones along the normal coordinates are best suited for the present purpose.

The potential energy surface of mode 4 in the excited state is determined from the experimental frequencies. The reason is that the vibrational wave function of this extremely flat energy surface is very sensitive for small inaccuracies in the energy surface. Moreover, the same equilibrium point Q_0 was taken for the ground and excited state. This is of course an approximation (see Table I) which was used to reduce the number of calculated points by a factor two. The effect of this approximation is that the sections made through the ex-

cited state potential energy surface are somewhat displaced when compared with the correct ones. This adversely affects all the excited state frequencies (see Table III), but in particular mode 4, because of the extremely small energy differences involved. The energy surface of mode 4 for the ground state and also the transition dipole moment and the vibrational overlap integrals, etc., between ground and excited state are of course obtained by calculation.

All quantities needed for the description of the radiative decay, with the exception of the ones mentioned above, were calculated on a level going beyond the "usual" approximations (e.g., harmonic vibrations, crude

Born–Oppenheimer states, analytical expressions for approximating Franck–Condon factors, etc.). Only in this way it is possible to describe the transitions on a level equivalent to the possibilities of the modern spectroscopic methods, as can be seen for instance, by comparing Lee’s spectrum³⁵ with our calculated results. It should be noted, that throughout this calculation the electronic wave functions and transition moments were explicitly calculated as functions of the normal coordinates, contrary to the conventional Herzberg–Teller approach, where one tries to include the Q dependence of electronic wave functions and properties by means of an expansion around Q_0 , i.e., an expansion in crude Born–Oppenheimer functions. Lin³⁶ recently published a calculation within the “normal” framework, in which he improved the classical work of Pople and Sidman.²⁷ Lin uses, however, the same MO’s as Pople and Sidman; these MO’s are not self-consistent, but the coefficients are roughly estimated. His work, which was mainly concerning the electronic dipole transition moment, gives results qualitatively differing from ours. This can be seen from Fig. 2, in which the modes 4, 5, and 6 are about equally important for inducing the radiative transition, while Lin’s calculation gives, that there are only two important modes, 4 and 6.

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