

ON THE $A^1\Pi-X^1\Sigma^+$ BAND SYSTEM IN CH^+ AND CD^+ : THEORETICAL SPECTROSCOPIC CONSTANTS AND LIFETIMES

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ABSTRACT

Polarization propagator calculation of spectroscopic constants and radiative lifetimes for the $A^1\Pi-X^1\Sigma^+$ band system are presented. The spectroscopic constants agree well with experimental and other theoretical values. We have also performed an iterative Rydberg-Klein-Rees (RKR) calculation of B_e , ω_e , and $\omega_e x_e$ for the experimental $X^1\Sigma^+$ state.

The calculated radiative lifetime for the $A^1\Pi$ state ($v' = 0$) is 660 ns and 598 ns, with theoretical and experimental potential energy curves, respectively. This difference (about 60 ns) indicates the inaccuracy in the present calculation. Experimentally the most recent estimate of the $A^1\Pi(v' = 0)$ state is 630 ± 50 ns, and theoretically the Yoshimine *et al.* transition moment gives $\tau(A^1\Pi, v' = 0) = 722$ ns.

The radiative lifetimes calculated for CD^+ are between 1.3% and 3.9% larger than the corresponding CH^+ lifetimes.

Subject headings: interstellar: molecules — laboratory spectra — molecular processes — transition probabilities

I. INTRODUCTION

The formation, destruction, and abundance of the CH^+ radical in interstellar space have been studied intensively in the last few years. The formation was first discussed by Bates and Spitzer (1951), and has also been treated by Smith, Liszt, and Lutz (1973) from a quantum-mechanical viewpoint. Based partly on observations by Herbig (1968), Solomon and Klemperer (1972) proposed that the CH^+ radical was a parent molecule in a number of two-body collision reactions forming diatomic molecules such as CH , C_2 , CO , and CN .

Early estimates of the interstellar abundance of CH^+ were based on assumed values for the oscillator strength of the resonance transition, $A^1\Pi-X^1\Sigma^+$, which is the only astronomically observed CH^+ band system (Douglas and Herzberg 1941; Douglas and Morton 1960). Thus Bates and Spitzer (1951) assumed that $f(0, 0) = 4 \times 10^{-3}$, while Solomon and Klemperer (1972) deduced the value 2.2×10^{-2} from the related transition in CH . Measurements of the radiative lifetime for the $A^1\Pi$ state (Smith 1971; Anderson, Wilcox, and Sutherland 1973; Brzozowski *et al.* 1974; Brooks and Smith 1975) give an experimental determination of the oscillator strength for the resonance transition. The variations among the different estimates of the radiative lifetimes are, however, considerable, and even the two latest measurements deviate by nearly a factor of 2. The measurements by Brzozowski *et al.* (1974) were performed on

individual rotational lines with a spectral resolution which was an order of magnitude better than previous work, and should be considered the most reliable. However, during the preparation of their manuscript, Erman (1977) informed us that the lifetimes given by Brzozowski *et al.* (1974) must be increased by 50% to 60% (see § IV) owing to a systematic error in the earlier CH^+ measurements. The error originates from the fact that the Coulomb repulsion among the CH^+ molecules tends to shorten the measured lifetimes. The new values for the lifetimes are approximately a factor of 3 larger than those reported by Brooks and Smith (1975).

Theoretically, the CH^+ radical has been studied by Green *et al.* (1972), Green, Hornstein, and Bender (1973), Yoshimine, Green, and Thaddeus (1973), Martin, Yeager, and McKoy (1974), and Watson, Stewart, and Dalgarno (1976). Green *et al.* performed a configuration interaction (CI) calculation of several potential energy curves and computed the $A-X$ transition moment. Martin, Yeager, and McKoy (1974) with an equations of motion (EOM) method, and Watson, Stewart, and Dalgarno (1976) with a time-dependent Hartree-Fock (TDHF) method, calculated excitation energies and oscillator strengths for a single internuclear distance which does not give spectroscopic constants. Further, since a lifetime determination requires knowledge of the vibrational wave functions, which in turn requires the electronic potential energy curves as a function of internuclear

distance, their results can be only qualitatively compared with the measured radiative lifetimes.

II. THEORY

In view of the still existing discrepancy between different estimates of the radiative lifetime of the $A\ ^1\Pi$ state of the CH^+ radical, we have undertaken a theoretical study of the $A\ ^1\Pi-X\ ^1\Sigma^+$ band system. Complete second-order polarization propagator calculations (Jørgensen 1975; Oddershede and Jørgensen 1977) were used to determine the excitation energies and transition moments for the resonance transition for 15 internuclear distances ranging from 0.8 to 2.1 Å. This method actually gives directly excitation energies and transition moments for a larger number of excited states; in the calculations here, up to 75 states of $^1\Sigma$ and $^1\Pi$ symmetry were obtained. The TDHF method used by Watson, Stewart, and Dalgarno (1976) is a special case of the polarization propagator approach, and the EOM method of Martin, Yeager, and McKoy (1974) differs from the second-order polarization propagator only in minor details. The method has been previously applied to similar problems in the SiO molecule by Oddershede and Elander (1976), to whom we will refer for further details. A comprehensive discussion of the second-order polarization propagator approximation can be found in Oddershede and Jørgensen (1977).

We have found, as in the case of SiO (Oddershede and Elander 1976), that the best description of the low-energy part of the CH^+ spectrum was obtained with a basis set where the core orbitals were given as single-zeta Slater-type orbitals (STO's) and the valence orbitals as optimized double-zeta STO's. Some diffuse STO's, especially on H, were added to give an improved description of the interatomic region. The complete basis set is given in Table 1.

TABLE 1
BASIS FUNCTIONS FOR CH^+ ,
 $\Phi_{nlm}(r, \Theta, \phi) = N_n r^{n-1} e^{-\zeta r} Y_{lm}(\Theta, \phi)$

n	l	m	Atomic Center	ζ
1.....	0	0	C	5.67263
2.....	0	0	C	1.83068
2.....	0	0	C	1.15282
2.....	1	0, ± 1	C	2.73045
2.....	1	0, ± 1	C	1.25656
3.....	0	0	C	0.6
3.....	1	0, ± 1	C	0.6
3.....	2	0, ± 1	C	0.6
1.....	0	0	H	1.33
1.....	0	0	H	2.47
2.....	0	0	H	0.9
2.....	1	0	H	0.8
2.....	1	0	H	0.2
2.....	1	± 1	H	1.15
3.....	0	0	H	0.7
3.....	1	0	H	0.5
3.....	1	± 1	H	0.3
3.....	1	± 1	H	0.6
4.....	0	0	H	0.2

III. SPECTROSCOPIC CONSTANTS

The polarization propagator approach does not at present give a ground-state total energy, and in order to determine spectroscopic constants, we thus require prior knowledge of the potential energy curve for *one* state, either from experiment, or from another theoretical calculation. The $A\ ^1\Pi$ state of CH^+ is experimentally better characterized than the $X\ ^1\Sigma^+$ state is, and we therefore consider the A state to be the more reliable reference state. However, in order to test the sensitivity of the computed quantities to the choice of the reference state, we have used both in our calculations. The potential energy curves and electronic transition moments determined here are also compared with the configuration interaction (CI) calculations of Green *et al.* (1972), which are the most accurate theoretical results currently available in the literature. Their ground-state curve is so close to the experimental curve in the region of interest that it is unnecessary to consider it as a third possible reference state. The second-order polarization propagator approximation uses a reference state consisting of the Hartree-Fock determinant plus all double excitations from it (Oddershede and Jørgensen 1977). We can therefore expect our method to be reliable only when this is a satisfactory description of physical reality, i.e., in the vicinity of the equilibrium geometry. This is the main reason for the deviation of our curve from the experimental one at large internuclear distances (see Fig. 1).

To get a reliable representation of the experimental ground-state potential energy curve for all the required R -values, we decided to perform an iterative RKR calculation of the $X\ ^1\Sigma^+$ state based on relative term values from Botterud, Lofthus, and Veseth (1973). The method, which accurately recalculates the relative term values, will be described in more detail elsewhere (Elander, Bunker, and Hehenberger 1977; Elander 1977). It is based on an idea of Stwalley (1972) that the rotationless potential energy curve can be improved by calculating RKR turning points for all known rotational and vibrational levels of an electronic state, instead of using extrapolated rotationless vibrational levels. A routine described by LeRoy (1977) was used to solve the radial Schrödinger equation. The spectroscopic constants ω_e , $\omega_e x_e$, and α_e are determined from the rotational and vibronic eigenvalues. Outside the range of the classical turning points, the potential was extended by fitting to Morse functions (Jarman 1971). The term values given by Botterud, Lofthus, and Veseth (1973) were used as initial estimates, and the final values are given in Table 2. The accuracy of the calculation is given by the sum of squares of the errors, 0.146 cm^{-1} , giving a rms error of 0.090 cm^{-1} , which is close to the spectroscopic accuracy. This does not, however, imply that the potential energy curve is of the same accuracy in the extrapolated region outside the range $0.70\text{--}1.80\text{ Å}$ (Elander 1977). The dissociation energy did not appear to be an important parameter in the fit, but it was

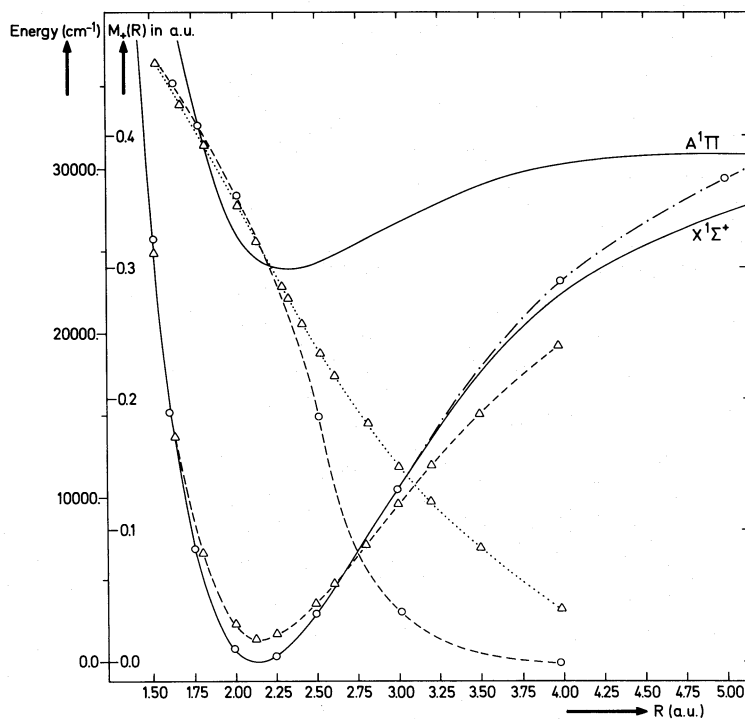


FIG. 1.—Potential energy curves and transition moments for the $A^1\Pi - X^1\Sigma^+$ transition in CH^+ . Solid curves, experimental RKR curves based on data from Botterud *et al.* (1973). The $X^1\Sigma^+$ potential energy curve and the $A^1\Pi - X^1\Sigma^+$ transition moment are plotted as determined from the present calculation (triangles) and from the calculation by Yoshimine *et al.* (1973) (circles).

necessary to include the anharmonic term $\omega_e y_e$ to get a good description of the ground state.

A least-squares fit of the ground-state *ab initio* curve of Green *et al.* (1972) to the Hulburt-Hirschfelder-Morse (HHM) model potential function (Hulburt and Hirschfelder 1941) does not reproduce their reported

TABLE 2
EXPERIMENTAL AND ITERATIVE RKR (IRKR) TERM
VALUES FOR THE $X^1\Sigma^+$ STATE OF CH^+

Vibrational Level (v)	Rotational Level (J)	Experiment (Botterud <i>et al.</i> 1973)	IRKR
0.....	0	0.02	-0.11
0.....	1	27.85	+27.76
0.....	2	83.51	+83.45
0.....	3	166.95	+166.92
0.....	4	278.05	+278.05
0.....	5	416.68	+416.72
0.....	6	582.66	+582.75
0.....	7	775.88	+775.96
0.....	8	995.96	+995.11
1.....	0	2739.69	+2739.78
1.....	1	2766.59	+2766.66
1.....	2	2820.30	+2820.37
1.....	3	2900.81	+2900.87
1.....	4	3007.99	+3008.04
1.....	5	3141.75	+3141.75
1.....	6	3301.87	+3301.85
1.....	7	3488.28	+3388.13
1.....	8	3700.53	+3700.37

r_e -value, which was obtained from a quartic polynomial fit to five points near the minimum. A cubic spline fit to their data was found unsatisfactory, since it gave unphysical oscillations. This is often found to be the case with spline fits when there are too few data points. Our calculations therefore include several additional points, and we have been able to obtain satisfactory fits of our derived potential curves to both HHM functions and spline functions. The computed constants from the iterative RKR method, from our curves, and from those of Green *et al.* are collected in Table 3 with the experimental values of Botterud, Lofthus, and Veseth (1973). The original paper of Green *et al.* (1972) did not give spectroscopic constants, but in a later paper Green, Hornstein, and Bender (1973) reported a Franck-Condon analysis and gave a table of their vibrational energy values. We have used these to determine the constants in Table 3 in the column labeled "their fit." The observation of marked anharmonicity in the A state by Douglas and Morton (1960) holds also for their results, and a vibrational energy expression including terms up to $\omega_e y_e$ is inaccurate for $v > 2$.

IV. RADIATIVE LIFETIMES OF THE $A^1\Pi$ STATE

The theory for radiative decay of excited electronic states in diatomic molecules has recently been reviewed by Hinze, Lie, and Liu (1975). We follow their notation. If the electronic transition moment, $M_e(R)$, is

TABLE 3
THEORETICAL AND EXPERIMENTAL SPECTROSCOPIC CONSTANTS IN cm^{-1} (r_e IN Å)
FOR THE $X^1\Sigma^+$ AND $A^1\Pi$ STATES IN CH^+

	THIS CALCULATION		GREEN <i>et al.</i> (1973)		EXPERIMENT	
	(a)	(b)	(b)	Their Fit	Iterative RKR	Botterud <i>et al.</i> (1973)
$X^1\Sigma^+$:						
r_e	1.146	1.141	1.140	1.130	1.1307	1.1295
B_e	13.81	13.93	13.95	14.20	14.1806	14.212
$\alpha_e \times 10^3$	0.57	0.63	0.42	...	0.487	0.490
ω_e	2604	2598	2806	2860	2879.83	...
$\omega_e x_e$	72.6	77.4	51	70	74.87	...
$\omega_e y_e$	1.3	2.3320	...
$\Delta G_{1/2}$	2459	2443	2704	2722	2737.7	2739.7
D_e	31205	31543	33187	33168	30300	...
$A^1\Pi$:						
T_e	22975.	22814.	25091.	24551.	...	24084.85
r_e	1.197	1.211	1.256	1.234	...	1.2360
B_e	12.65	12.35	11.49	11.91	...	11.8686
$\alpha_e \times 10^3$	0.72	0.52	0.82	0.937
ω_e	2306	2335	1709	1935*	...	1838.2
$\omega_e x_e$	91	71	88	125*	...	100.0
$\Delta G_{1/2}$	2124	2193	1533	1685	...	1638.2
D_e	11186	8322	8674

(a) Using a spline fit to the calculated points.

(b) Using a Hulburt-Hirschfelder-Morse fit to the calculated points.

* Holds only for $v = 0, 1, 2$.

given in atomic units and the excitation energy in cm^{-1} , then the radiative lifetime, $\tau_{n'v'J'}$, of an electronic (n') vibrational (v') and rotational (J') level $|n'v'J'\rangle$ is

$$\tau_{n'v'J'}^{-1} \text{ (ns)} = 2.02607 \times 10^{-15} \sum_{n''v''J''} \sigma^3(n'v'J', n''v''J'') \times \langle n'v'J' | M_e(R) | n''v''J'' \rangle^2 S_{J''J'} / (2J' + 1), \quad (1)$$

as given by Oddershede and Elander (1976). $\sigma(n'v'J', n''v''J'')$ is the excitation energy,

$$\langle n'v'J' | M_e(R) | n''v''J'' \rangle$$

the total transition moment, and $S_{J''J'}$ are the line strengths or Höln-London factors. We refer to the latter reference for a description of the calculational method used in the present investigation.

The calculated $A^1\Pi-X^1\Sigma^+$ electronic transition moment is plotted in Figure 1. We found in the present calculation as well as in the study of the resonance transition of SiO (Oddershede and Elander 1976), that $M_e(R)$ was rather insensitive to variations in the basis set, whereas the excitation energies could change as much as 0.5 eV with moderate changes in the valence orbital exponents. The smooth behavior of $M_e(R)$ indicates that the $A^1\Pi$ state is well separated from all other states which have dipole allowed transitions to the ground state. $M_e(R)$ goes to zero at

TABLE 4
VIBRATIONAL LIFETIMES (in ns) FOR THE $A^1\Pi$ STATE IN CH^+ CALCULATED WITH VARIOUS POTENTIAL ENERGY CURVES

v'	YOSHIMINE <i>et al.</i> (1973)		THIS CALCULATION BASED ON $A^1\Pi$			EXPERIMENTAL		
	(a)	(b)	(a)	(b)	(c)	(d)	(e)	(f)
0.....	722	738	660	567	598	408 ± 30	250 ± 75	630 ± 50
1.....	780	847	776	672	711	495 ± 50	270 ± 75	750 ± 60
2.....	855	963	922	802	845	530 ± 50	290 ± 75	850 ± 70
3.....	970	1114	1113	975	1010	465 ± 50
4.....	525 ± 50

(a) Calculated value using theoretical transition moment and potential energy curves (see Fig. 1).

(b) As (a) except that the experimental T_e -value from Botterud *et al.* (1973) is used to scale the potential energy curves.

(c) Calculated from theoretical transition moments and experimental RKR curves based on data from Botterud *et al.* (1973).

(d) Brzozowski *et al.* (1974).

(e) Brooks and Smith (1975), no error bar given in the reference for the $v' = 0$ level.

(f) Private communication from Erman (1977).

large R -values, since the $A^1\Pi$ and the $X^1\Sigma^+$ states have identical dissociation limits, $C^+(^2P) + H(^2S)$.

The transition moment from the present calculation follows the one given by Yoshimine, Green, and Thaddeus (1973) very closely up to the equilibrium internuclear distance (1.13 Å), after which their $M_e(R)$ -value approaches zero faster than ours. This is reflected in a similar variation in the calculated radiative lifetimes in Table 4. The effect can best be observed if we use the same potential energy curves—the experimental RKR curves (see column [c] in Table 4). We find, as expected, that the transition moment of Yoshimine, Green, and Thaddeus (1973) gives longer lifetimes and furthermore lifetimes which, due to the “earlier” leveling off of their $M_e(R)$, vary less with the vibrational quantum number, v' .

The other columns in Table 4 show a similar type of behavior, but the variations in the spectroscopic constants (see Table 3) do influence the calculated radiative lifetimes. The size of T_e especially is important because of the third-power energy-dependence of τ .

Comparison of columns (a) and (b) in Table 4 gives an indication of the dependence of τ on T_e , and the difference between columns (b) and (c) indicates the influence on τ of inaccuracies in the potential energy curves. Franck-Condon factors, $q(v', v'')$, were also calculated to check the convergence in the sum over v'' in equation (1). If

$$\sum_{v''} q(v', v'') \geq 0.99,$$

the calculation was considered to have converged. For $v' = 0, 1$, and 2, convergence was easily obtained, and also in most cases for $v' = 3$, whereas the $v' = 4$ level never fulfilled the above criterion and results for $v' = 4$ are therefore not included in Table 4.

Summarizing, we can state that the two theoretical calculations agree quite well in their prediction of the radiative lifetime for the $A^1\Pi$ state. The purely theoretical results, those in columns (a) of Table 4, and the radiative lifetimes in which various degrees of experimental information about the potential energy curves are included (columns [b] and [c] in Table 4) indicate that $\tau(A^1\Pi)$ should be between 600 and 700 ns (for $v' = 0$), with our calculated results near the lower end of the range and the results of Yoshimine, Green, and Thaddeus (1973) at the higher end.

The lifetimes measured by Brzozowski *et al.* (1974) are approximately a factor 2/3 smaller than our calculated values for $v' = 0, 1, 2$ (see Table 4). However, during the course of this work, Erman (1977) discovered that a systematic error was present in their earlier measurements. The Coulomb repulsion between the positive CH^+ ions removes a fraction of them from the reaction chamber, causing a decrease in the measured macroscopic intensity that results in too small values for the radiative lifetimes. This effect can be compensated for by introducing low-energy electrons by a technique discussed in detail by Curtis and Erman (1977).

The results of Brooks and Smith (1975) are a factor of 2.5–3 times shorter than those from the present

calculation. They report lifetimes for $v' = 0, 1, 2$ of 250, 270, and 290 ns, respectively.

We have also investigated the variations of $\tau(A^1\Pi)$ with the vibrational quantum number, v' , for the $A^1\Pi$ state. This is done in Figure 2, where we have plotted the ratio between $\tau_{v'}$ and τ_0 . For $v' = 0, 1, 2$, both calculated and experimental results (Brzozowski *et al.* 1974; Brooks and Smith 1975) show a similar behavior, whereas the measurements by Brzozowski *et al.* for $v' = 3$ and 4 do not fit the calculated pattern even if we include the experimental error bars. We find it hard to place these high v' measurements into any pure radiative decay pattern, which may indicate an interaction with a nonradiative state lying near the higher vibrational levels of the $A^1\Pi$. Similar predissociative effects have actually been observed in the NH molecule by Smith, Brzozowski, and Erman (1976) and in the NO molecule by Brzozowski, Erman, and Lyyra (1976). There seem, however, not to be any CH^+ states which can cause this predissociation, and a more plausible explanation for the decrease in the radiative lifetime is blends from the more intense $A^2\Pi$ band in CH (Erman 1977).

The variation of $\tau(A^1\Pi)$ with the rotational quantum number J' is plotted in Figure 3, calculated with

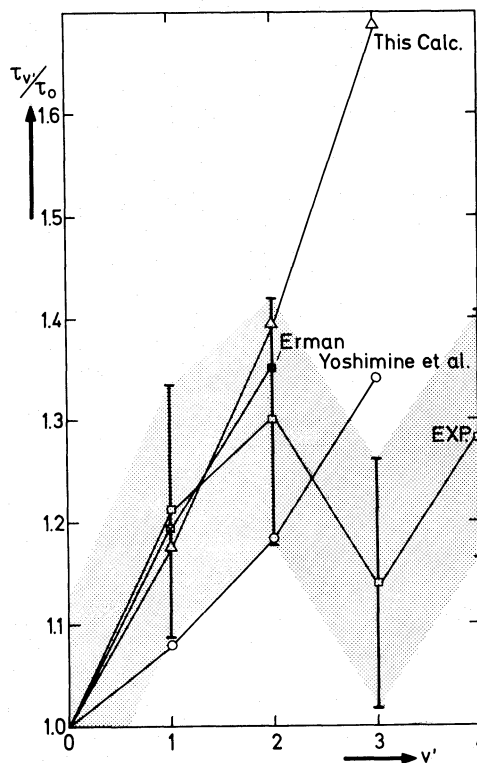


FIG. 2.—The vibrational radiative lifetimes of the $A^1\Pi$ state relative to the zero vibrational level as obtained from the present calculation (triangles), from Yoshimine *et al.* (1973) (circles), from Erman (1977) (squares with a cross), and from the experiments (squares) by Brzozowski *et al.* (1974) and Brooks and Smith (1975). The shaded area indicates the uncertainties on the experimental results.

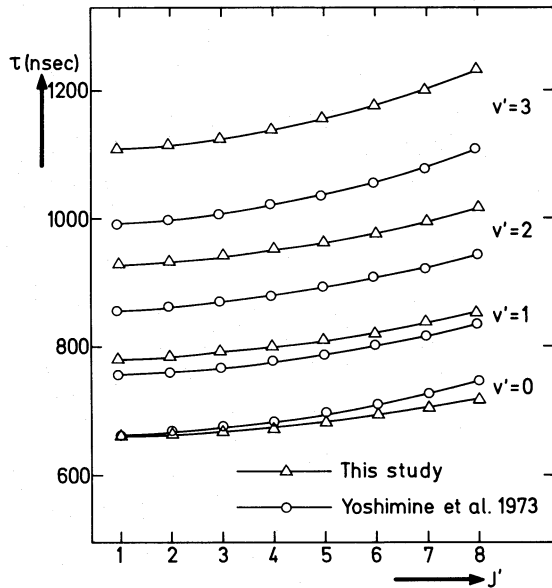


FIG. 3.—The calculated radiative lifetimes for the $A^1\Pi$ state as a function of the rotational, J' , and vibrational, v' , quantum numbers. The lifetimes from the present calculation (triangles) and the calculation by Yoshimine *et al.* (circles) are renormalized to agree with our calculation for $v' = J' = 0$.

both ours and the Yoshimine, Green, and Thaddeus (1973) electronic transition moments. The lifetimes in Figure 3 are scaled to fit our calculated lifetime (660 ns) for $v' = 0$. The motivation for calculating $\tau(J')$ was to get an estimate of errors in the experimental measurements in which the radiative lifetime is obtained as an average over several rotational components (Brzozowski *et al.* 1974). The variation with J' is smallest for $v' = 0$, about 60 ns for $1 \leq J' \leq 8$, and increases to about 130 ns for the same J' range

for $v' = 3$. This indicates that the inaccuracies in $\tau_{v'J'}(A^1\Pi)$ due to J' variations of the lifetimes are inside the error bars given by Erman (1977).

In a study of SiO, Oddershede and Elander (1976) found that the lifetimes calculated in the R -centroid approximation (Jarman and Fraser 1953) were very close to those calculated using the exact expressions. For CH^+ we find similarly that $\tau(A^1\Pi, v' = 0) = 651$ ns in the R -centroid approximation, compared with the "exact" result of 661 ns. If we assume that $M_e(R) = M_e(R_0)$ where R_0 is the R_e -value for the $A^1\Pi$ state, the calculated lifetime becomes 567 ns, i.e., about 100 ns too low. This error is of importance when estimating the accuracy of experimental band absorption oscillator strengths, since these are obtained from the measured radiative lifetimes by using the above approximation. A strict comparison between the theoretical and experimental band oscillator strengths, $f(v', v'')$, in Table 5 is therefore not possible. We see, however, that the two different theoretical methods agree very well for most (v', v'') values. Furthermore, the quantity $f(v', v'')/q(v', v'')$ from the present calculation varies in a manner similar to that found by Yoshimine, Green, and Thaddeus (1973). This ratio is often referred to as "the electronic oscillator strength," f_{el} (see, e.g., Oddershede and Elander 1976). For the v' range 0 to 2 we find that $f_{el} = 0.017 \pm 0.005$ ($v'' = 0$), and $f_{el} = 0.010 \pm 0.004$ ($v'' = 1$) where the error bars indicate the maximum deviation in this v' range. The corresponding electronic oscillator strengths from the Yoshimine, Green, and Thaddeus (1973) data are $f_{el} = 0.017 \pm 0.007$ ($v'' = 0$) and $f_{el} = 0.009 \pm 0.004$ ($v'' = 1$).

The ratio between $f(1, 0)$ and $f(0, 0)$ is 0.57 compared with 0.67 from Yoshimine, Green, and Thaddeus (1973). The best interstellar data indicate that this ratio should be around 0.61 (see the paper by Yoshimine, Green, and Thaddeus [1973] for a detailed discussion of this point).

TABLE 5
BAND ABSORPTION OSCILLATOR STRENGTHS $f(v', v'')$ FOR THE $A^1\Pi(v')-X^1\Sigma^+(v'')$ BAND SYSTEM IN CH^+

v'	v''	THEORETICAL		"EXPERIMENTAL" ^a	
		Yoshimine <i>et al.</i> (1973)	This Work ^b	Brzozowski <i>et al.</i> (1974)	Brooks and Smith (1975)
0.....	0	0.00645	0.00743	0.0115 ± 0.0016	0.016
1.....	0	0.00431	0.00426	0.00555	0.0107
2.....	0	0.00173	0.00170	...	0.0043
3.....	0	...	0.00063
0.....	1	0.00097	0.00176
1.....	1	0.00110	0.00120
2.....	1	0.00306	0.00327
3.....	1	...	0.00278
0.....	2	...	0.00026
1.....	2	...	0.00170
2.....	2	...	0.00004
3.....	2	...	0.00005

^a This is not a directly measurable quantity (see text).

^b Computed from the calculated transition moment and experimental RKR potential curves.

V. ISOTOPE EFFECTS IN RADIATIVE LIFETIMES

Relative and absolute measurements of lifetimes of corresponding levels in isotopic molecules have recently appeared in the literature (Brzozowski, Erman, and Lew 1975). In the Born-Oppenheimer approximation the electronic transition moments and potential energy curves are independent of the nuclear masses. It is thus possible to calculate the radiative lifetime for the $A^1\Pi$ state in CD^+ by simply changing the reduced mass from μ_{CH^+} to μ_{CD^+} in the nuclear Schrödinger equation. Results are given in Table 6.

The only measurement of radiative lifetimes for CD^+ (Smith 1971) disagrees seriously with the present calculation, with respect to both the absolute value of the lifetime, and the trend in the isotope shift. Smith (1971) finds that $\tau(CD^+)$ is less than $\tau(CH^+)$, which is the opposite variation of that found in the present calculation. The uncertainties in the above measurements are, however, too large (see, e.g., Brooks and Smith 1975) to justify any firm conclusion concerning the trend of the isotope shifts. The measurements on OH^+/OD^+ and H_2O^+/D_2O^+ by Brzozowski, Erman, and Lew (1975) show the same tendency as that found for CH^+/CD^+ in the present investigation. The relative isotope shift is somewhat larger, namely, 10.8%–13.5% for H_2O^+/D_2O^+ and 8.9% for OH^+/OD^+ . The high-frequency deflection technique results for these ions are also influenced by the Coulomb repulsion effects discussed for CH^+ . This problem does however not affect the relative isotope shift; only the absolute values are changed (Curtis and Erman 1977).

There are three important features which affect the isotope shift of the vibronic lifetime:

i) If the electronic transition moment is constant over the internuclear distances for which the vibrational overlap is large, the variation in lifetime is due only to the change in the transition energy, σ (see eq. [1]). According to Herzberg (1950), the difference in term values for a given state is

$$G_{CH^+}(v) - G_{CD^+}(v) = (1 - \rho)\omega_e(v + \frac{1}{2}) - (1 - \rho^2)\omega_e x_e(v + \frac{1}{2})^2 \quad (2)$$

TABLE 6
VIBRATIONAL LIFETIMES (in ns) FOR THE $A^1\Pi$
STATE OF CD^+

v'	Theoretical Potential Energy Curves		Experimental RKR Curves	$\frac{\tau_{CD^+} - \tau_{CH^+}}{\tau_{CH^+}} \times 100$
	(a)	(b)	(c)	(d)
0.....	681	572	606	1.3
1.....	815	685	736	3.5
2.....	967	813	878	3.9
3.....	1144	965	1030	2.0

(a), (b), and (c) are as defined in Table 4.

(d) Using the lifetimes in column (c) of this table and Table 4.

where

$$\rho = \left(\frac{\mu_{CH^+}}{\mu_{CD^+}} \right)^{1/2}. \quad (3)$$

Including only terms linear in ρ , the difference in the $X^1\Sigma^+ - A^1\Pi$ transition energy, $\Delta\sigma(v', v'')$ for CH^+ and for CD^+ becomes

$$\Delta\sigma(v', v'') = \sigma_{CH^+} - \sigma_{CD^+} = (1 - \rho)[\frac{1}{2}(\omega_e' - \omega_e'') + \omega_e'v' - \omega_e''v''], \quad (4)$$

where the double-primed quantities refer to the ground state and the primed quantities to the $A^1\Pi$ state, and where we have used the fact that T_e is the same for CH^+ and CD^+ in the Born-Oppenheimer approximation. Since $\rho < 1$ and $\omega_e' < \omega_e''$, $\Delta\sigma(0, v'')$ must always be negative. For other v' values $\Delta\sigma$ can be both positive and negative. Table 7 contains some typical values for the CH^+/CD^+ molecules.

ii) Qualitatively, the total transition moment is proportional to the square of the vibrational overlap of the initial and final vibronic levels weighted by the electronic transition moment. In the case of CH^+ , the transition moment decreases with increasing internuclear distance. When the proton is substituted by a deuteron, the term values decrease (see eq. [2]) and the left turning point of the vibrational wave function moves to the right (toward larger internuclear distance) and the right turning point moves to the left. Since the transition moment is larger at the left turning point than at the right, deuteration should thus on the basis of this effect alone lead to a decrease of the vibronic transition moment.

iii) Variations in the Franck-Condon factors will also influence the total transition moment. The vibrational overlap depends heavily upon the relative position of the turning points in the upper and lower states. The more different ω_e' , r_e' and ω_e'' , r_e'' are, the more will the relative position of the turning points change with an isotope substitution which again implies substantial changes in $q(v', v'')$. For the CH^+/CD^+ molecules, the $X^1\Sigma^+$ and $A^1\Pi$ states are rather different, and we do find a large change in $q(v', v'')$ going from CH^+ to CD^+ (see Table 7).

From the quantities in Table 7, it is apparent that points (iii) above causes the most important isotope shift in the radiative lifetime of the $A^1\Pi$ state in CH^+/CD^+ . The changes in $CH^+ \rightarrow CD^+$ transition moments (and τ^{-1}) show the same trends as the changes in the corresponding Franck-Condon factors. Only for $(v', v'') = (1, 0)$ is (ii) the dominate effect which, together with the decrease in σ^3 (point [i]), actually is responsible for the larger isotope shift for $v' = 1$ than for $v' = 0$ (see Table 6).

It is difficult to intuitively predict changes in Franck-Condon factors owing to isotopic substitutions, whereas one has a better feeling for the changes in electronic transition moments and excitation energies. It is therefore unfortunate that point (iii) seems to give the dominant isotope effect when the upper and lower potential curves are different, since this makes an

TABLE 7
ISOTOPE SHIFTS^a IN TRANSITION ENERGIES, $\sigma(v', v'')$, FRANCK-CONDON FACTORS, $q(v', v'')$, TRANSITION MOMENTS, $M(v', v'')$, AND RADIATIVE LIFETIMES, $\tau_{v',v''}$ FOR THE $A^1\Pi-X^1\Sigma^+$ BAND SYSTEM IN CH^+/CD^+

		CH^+					CD^+				
v'	v''	$\Delta\sigma^b$ cm^{-1}	$\sigma^3 \times 10^{-13}$ cm^{-3}	q	$M^2 \times 10^2$ au	τ^{-1} μs	$\sigma^3 \times 10^{-13}$ cm^{-3}	q	$M^2 \times 10^2$ au	τ^{-1} μs	
0.....	0	-152	1.316	0.628	5.18	1.382	1.342	0.505	4.19	1.138	
0.....	1	-854	0.909	0.283	1.08	0.255	1.026	0.350	2.08	0.433	
0.....	2	-1499	0.609	0.074	0.23	0.029	0.772	0.110	0.44	0.079	
0.....	3	-2092	0.392	0.013	0.03	0.002	0.570	0.029	0.09	0.010	
1.....	0	+243	1.610	0.260	2.78	0.906	1.564	0.275	2.73	0.863	
1.....	1	-459	1.141	0.119	0.89	0.207	1.212	0.017	0.13	0.031	
1.....	2	-1103	0.788	0.328	1.40	0.224	0.927	0.285	1.60	0.293	
1.....	3	-1697	0.528	0.208	0.56	0.060	0.698	0.251	0.92	0.131	
1.....	4	-2238	0.340	0.070	0.12	0.008	0.516	0.122	0.33	0.035	
1.....	5	-2720	0.210	0.016	0.02	0.001	0.374	0.041	0.08	0.006	

^a Computed from the calculated transition moment and experimental RKR potential curves.

^b Defined in eq. (4).

a priori estimate of isotope shift rather difficult. The r_e -values for the $X^3\Sigma^-$ and the $A^3\Pi$ states of OH^+ are more different than those for the $X^1\Sigma^+$ and $A^1\Pi$ in CH^+ (Herzberg 1950; Liu and Verhagen 1971), whereas the ω_e -values are more similar (Rakotoarijimy 1969, 1970). This should indicate that the isotope shift in CH^+/CD^+ and OH^+/OD^+ is of the same size, which is in agreement with the measurements of Brzozowski, Erman, and Lew (1975). The slightly larger shift in OH^+/OD^+ may be explained by the larger r_e difference between ground and excited states.

Recently Gérard *et al.* (1976), from comparison between experimental emission branching ratios and those calculated in the R -centroid approximation, found a variation in the electronic transition moment for OH^+/OD^+ very similar to that for CH^+/CD^+ in Figure 1. They have also calculated the isotope shift in the radiative lifetime for OH^+/OD^+ , and they find a smaller shift than that reported by Brzozowski, Erman, and Lew (1975).

VI. SUMMARY

We have presented polarization propagator calculation of spectroscopic constants and radiative lifetimes for the resonance transition in CH^+ . The spectroscopic constants from the present investigation agree well with other experimental (Botterud, Lofthus, and Veseth 1973) and theoretical values (Green *et al.* 1972; Green, Hornstein, and Bender 1973).

The radiative lifetimes are the primary output from emission experiments. The calculation of the lifetime for the $A^1\Pi$ state gives therefore a *direct* way to compare theory and experiment. We found that the lifetimes from the present calculation are in excellent agreement with the recent results of Erman (1977) but somewhat larger than those measured by Brzozowski *et al.* (1974) and considerably larger than the phase-shift results by Brooks and Smith (1975).

We found good agreement between the lifetimes from the present investigation and those calculated using the Yoshimine, Green, and Thaddeus (1973) electronic transition moment. The two theoretical methods are quite different, and the harmony between the calculated lifetimes in the two methods increases the reliability of the theoretical prediction of the interstellar abundance of CH^+ . For a further analysis of the astrophysical consequences of the present calculations, we refer to the papers by Yoshimine, Green, and Thaddeus (1973) and Brzozowski *et al.* (1974), since their conclusions will not change much when our calculated transition moments are used.

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