Predissociation lifetimes of the $E\ ^2\Pi$ and $F\ ^2\Pi$ states of CH

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Abstract

Using the Golden Rule approximation, the predissociation lifetime of the $v = 0$ vibrational level of the CH ($E\ ^2\Pi$) state, due to its strong avoided crossing with the CH ($F\ ^2\Pi$) state, was found to be of the order of $\tau_{pre} \approx 2$ ps. This agrees well with the recent rotationally resolved experimental lifetimes. As expected, higher vibrational levels of the E and F states are extremely short-lived, having a τ_{pre} of the order of a few fs. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Much work has been done on the CH radical due to its simplicity and importance. Recently, accurate calculations of many states of CH have been reported, and references to numerous experimental and theoretical papers have been given [1]. Most of the known excited states of CH predissociate either due to radial or spin–orbit or rotational coupling or due to barrier penetration.

Here, we are particularly interested in the states $E\ ^2\Pi$ and $F\ ^2\Pi$, which undergo a strong avoided crossing around 2.58 bohr. Notice that in the past, these states had been referred to as $D\ ^2\Pi$ and $E\ ^2\Pi$, respectively, because of the missing lower $D\ ^2\Sigma^+$ state, the existence of which has only recently been established [1]. The E state has been observed during the flash photolysis of diazome-thane [2] and by multiphoton ionization techniques [3,4]. The presence of predissociation is expressed by the diffuseness of the absorption lines. Experimental predissociation lifetimes of various rotational levels of the E state have been obtained by the two-color resonant four-wave mixing technique [5]. A low accuracy estimate of the predissociation rate of CH due to radial coupling after excitation to the E, F and $H\ ^2\Pi$ states has been reported within the context of its photodissociation mechanisms [6]. The purpose of this paper is to estimate the predissociation lifetimes of a few vibrational levels of these states due to their avoided crossing, and to compare them with the experimental work mentioned above.

2. Methodology and results

We have performed the ab initio calculations of the potential energies and wave functions of the first four $^2\Pi$ states of CH using the MRDCI

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package [7–11]. From a relatively small preselected set of configurations (up to 50 000 for our current version), this package can calculate the energies to near full CI accuracy by an extrapolation technique. We have set the origin of the coordinate system on the center of mass of CH. As a basis set, we have used the correlation consistent aug-cc-pVTZ basis set of Dunning and coworkers [12,13], which contains enough diffuse functions to calculate reliably these states. The results are shown in Table 1. The ab initio values of the E and F potential energies in Table 1 have been fitted to quadratic polynomials via a segmented least-squares procedure for later use. The result is depicted in Fig. 1.

For estimating the predissociation rate due to the avoided crossing of the E and F states we have employed the Golden Rule approximation

$$k_{pre} = (2\pi/\hbar)|\langle b|U|a\rangle|^2 \rho_b(E), \tag{1}$$

where $|a\rangle$ is the discrete vibrational state with energy E, $\langle b|$ is the continuous state at E and $\rho_b(E)$ is the density of the continuous states around E. In what follows $\rho_b(E)$ is absorbed in the continuous

radial wave function, which is energy normalized. U is the radial coupling given here by

$$U(R) = -(\hbar^2/2\mu)B(R) - 2(\hbar^2/2\mu)A(R)\partial/\partial R,$$

with $B(R) = \langle \Psi_f|\partial^2/\partial R^2|\Psi_i\rangle$, and $A(R) = \langle \Psi_f|\partial/\partial R|\Psi_i\rangle$, which are essentially the B.O. neglected terms. Ψ_i and Ψ_f are the adiabatic initial (bound) and final (dissociative) electronic wave functions of the states undergoing the avoided crossing. $A(R)$ has been obtained (vide infra) and the rest of the calculation has proceeded numerically using a constant grip with step size h everywhere. The numerical integration in (1) has been done simply by the trapezoidal rule using a small h.

The Golden Rule approximation is valid only for small transition rates, that is for small radial couplings. If the adiabatic radial coupling is indeed small, one should use the adiabatic representation, thus determining the lifetime of the bound adiabatic state. If the adiabatic radial coupling is strong, the diabatic coupling must be small. Then one should use the diabatic representation, thus determining the lifetime of the bound diabatic state.

Table 1
CH ab initio energies (in a.u.) shifted by 38.00 a.u. (R_{CH} in bohr)

R_{CH}	$X\,^2\Pi$	$E\,^2\Pi$	$F\,^2\Pi$	$H\,^2\Pi$
1.6	−0.3403	−0.0590	−0.0373	−0.0295
1.8	−0.3894	−0.1119	−0.0882	−0.0818
2.0	−0.4075	−0.1338	−0.1089	−0.1022
2.2	−0.4087	−0.1377	−0.1150	−0.1046
2.3	−0.4057	−0.1355	−0.1155	−0.1021
2.4	−0.4021	−0.1327	−0.1170	−0.0974
2.45	−0.3987	−0.1299	−0.1170	−0.0929
2.5	−0.3965	−0.1277	−0.1191	−0.0909
2.55	−0.3934	−0.1255	−0.1208	−0.0924
2.56	−0.3927	−0.1252	−0.1211	−0.0926
2.57	−0.3921	−0.1251	−0.1213	−0.0927
2.58	−0.3914	−0.1252	−0.1212	−0.0928
2.6	−0.3900	−0.1261	−0.1206	−0.0929
2.62	−0.3887	−0.1274	−0.1196	−0.0929
2.65	−0.3868	−0.1299	−0.1179	−0.0928
2.7	−0.3835	−0.1344	−0.1148	−0.0921
2.75	−0.3793	−0.1384	−0.1104	−0.0908
2.8	−0.3764	−0.1441	−0.1080	−0.0897
2.9	−0.3695	−0.1538	−0.1009	−0.0864
3.0	−0.3625	−0.1629	−0.0936	−0.0828
3.2	−0.3464	−0.1765	−0.0754	−0.0716
3.4	−0.3337	−0.1902	−0.0661	−0.0614
3.6	−0.3227	−0.2007	−0.0620	−0.0483
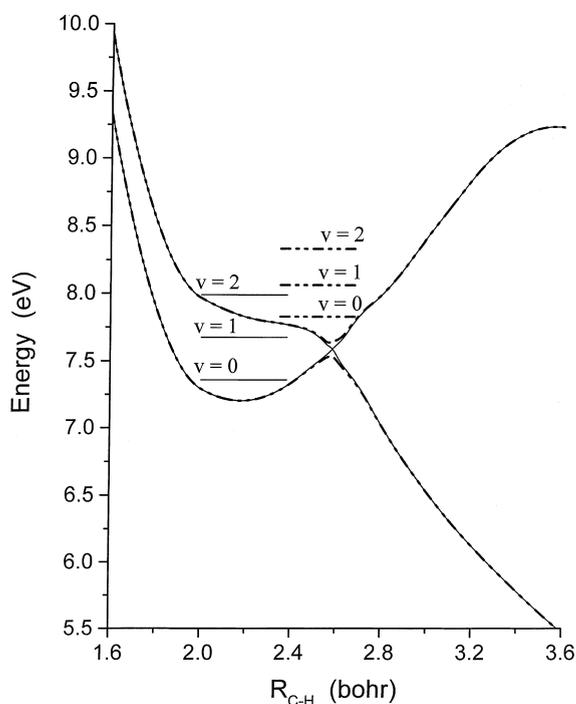
Fig. 1. The $E\ ^2\Pi$ and $F\ ^2\Pi$ adiabatic (dashed-dotted-dotted lines) and the diabatic (solid lines) potential energy curves of CH scaled to the minimum of the ground state energy (-38.4097 a.u.). The corresponding $v = 0$, 1 and 2 vibrational levels are also shown.

Table 2
The ab initio computed $A(R)$ matrix elements

R_{CH} (bohr)	$A(R)$ (1/bohr)	R_{CH} (bohr)	$A(R)$ (1/bohr)
2.30	0.282	2.60	11.8
2.40	0.520	2.62	6.47
2.50	1.99	2.65	2.62
2.55	7.91	2.70	0.968
2.56	10.9	2.80	0.730
2.58	16.3	2.90	0.362
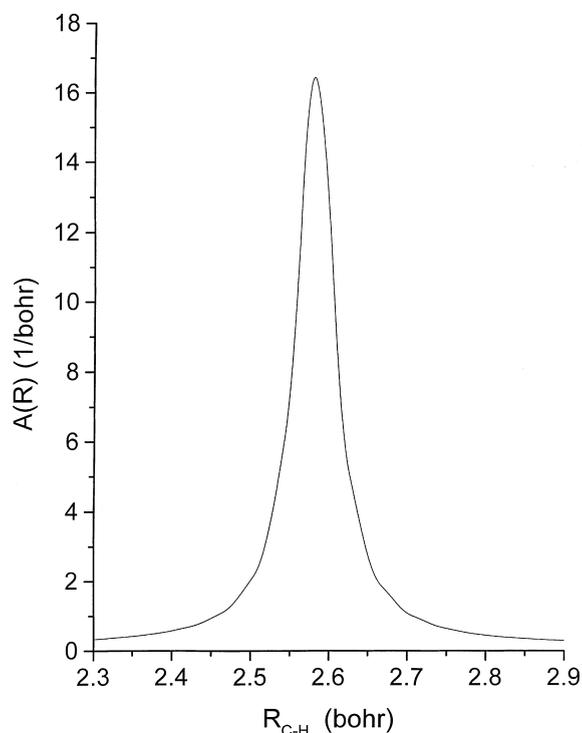
Fig. 2. The adiabatic radial coupling between the $E\ ^2\Pi$ and $F\ ^2\Pi$ adiabatic states of CH.

In either case one must calculate the radial couplings $B(R)$ and $A(R)$. The $A(R)$ term has been obtained by a finite differences method which involves computing the energies and the wave functions at two nearby points (usually about 0.002 bohr apart) with the origin of the coordinate system set on the center of mass [14]. Notice that the MRDCI energy extrapolation technique does not extend to the wave functions. In order to obtain reliable d/dR matrix elements the selection threshold must allow the selection of at least 40 000–50 000 configurations so that the wave functions can be calculated with as much accuracy as possible. The computed $A(R)$ matrix elements are shown in Table 2. These values have been fitted to a Lorenzian function, and the corresponding graph is shown in Fig. 2. The area under the curve is very close to $\pi/2$ (about 1.51) as expected. The $B(R)$ term is usually neglected since it is much smaller than the $A(R)$ term. If it has to be included, it can be reasonably approximated as the derivative of $A(R)$. Once k_{pre} is estimated the lifetime and width are obtained by the relations $\tau_{pre} = 1/k_{pre}$ and $\Gamma_{pre} = \hbar/\tau_{pre}$, where $\hbar = 5.3089 \times 10^{-12}\ cm^{-1}$ s.

2.1. Adiabatic representation

For this case, and neglecting the $B(R)$ term, the Golden Rule expression takes the form (in atomic units)

$$k_{pre}^{a} = 4.1341 \times 10^{16}(2\pi/\mu^2)|\langle\chi_f|A(R)\hat{\partial}/\partial R|\chi_i\rangle|^2 \ s^{-1},$$
(2)

where the numerical factor converts the rate from atomic units of time to seconds, μ is the reduced mass, χ_i and χ_f are the initial (discrete) and final (continuous) radial wave functions. The desired vibrational levels and radial wave functions are calculated as we will show later using the potential fits shown in Fig. 1. The numerical differentiation in (2) is done by finite differences.

2.2. Diabatic representation

The theory of the two-state adiabatic to diabatic orthogonal transformation is well known [15,16]. Its main points as applied here have been given previously [17]. The resulting diabatic potentials are in numerical form on the constant grid. Fig. 1 depicts these potentials along with the adiabatic ones. The Golden Rule expression for the diabatic states takes the form (in atomic units)

$$k_{pre}^{d} = 4.1341 \times 10^{16}(2\pi)|\langle\zeta_f(R)|W(R)|\zeta_i(R)\rangle|^2 \ s^{-1},$$
(3)

where again the numerical factor converts the atomic units of time to seconds. The U in (1) has now been replaced by the diabatic *potential* coupling $W(R)$. The integral is non-zero as opposed to the integral of the diabatic *momentum* coupling (d/dR), which is zero (by construction). The transformation gives $W(R)$ in numerical form on the constant grid. Of course only the values around the crossing are non-zero (practically). ζ_i and ζ_f are the initial (discrete) and final (continuous) radial wave functions referring to the diabatic potentials.

2.3. Numerical calculations

In both representations the calculation of the vibrational energy levels of the bound state has been done here by a modified Numerov algorithm [18]. The radial continuous wave function of the dissociative state at the vibrational energy of the bound state has been calculated using a three-point iterative procedure [19]. The numerical form of it on the constant grid is given by

$$[1 - T(R + h)]\xi_f(R + h)$$
$$= [2 + 10T(R)]\xi_f(R) - [1 - T(R - h)]\xi_f(R - h),$$
(4)

where $T(R) = (2/3)\mu\pi^2[V(R) - E]$ and $V(R)$ is either the adiabatic ($\xi = \chi$) or the diabatic ($\xi = \zeta$) potential depending on the employed representation. E is the energy of the bound state. The first two values of the function must be supplied as it has been suggested [20]. We have started the iteration with $\xi_f(R - h) = 0.000$ and $\xi_f(R) = 0.0001$. The starting value of the second point has been determined by supplying gradually decreasing values of it until the final result remained practically unchanged. This continuous wave function has been energy normalized by fitting it to the asymptotic form (evaluated at some distant R)

$$\xi_\infty(R) = (2\mu/\pi\kappa)^{1/2}\kappa R[\cos(\delta_l)j_\ell(\kappa R) - \sin(\delta_l)\eta_l(\kappa R)],$$
(5)

where δ_l is the phase shift and $\kappa = (2\mu E)^{1/2}$. For $l = 0$ this becomes $\xi_\infty(R) = (2\mu/\pi\kappa)^{1/2} \times \sin(\kappa R + \delta_0)$. The estimate of the phase shift is based on the assumption that at some asymptotic distances R_1 and R_2 the ratio of the values of the wave function taken either from (4) or from (5) must be the same since the function computed from (4) must fit asymptotically the function computed from (5). That is $\xi_f(R_1)/\xi_f(R_2) = \Xi = \xi_\infty(R_1)/\xi_\infty(R_2)$, with Ξ computed from the known values of $\xi_f(R_1)$ and $\xi_f(R_2)$. Then from (5) and for $l = 0$ one obtains

$$\tan(\delta_0) = [\Xi \sin(\kappa R_2) - \sin(\kappa R_1)]$$
$$\times [\cos(\kappa R_1) - \Xi \cos(\kappa R_2)]^{-1}.$$

The normalization factor is taken as the ratio $\xi_\infty(R)/\xi_f(R)$ computed iteratively at large R's until it remains constant within a preset tolerance (10^{-3} here). The predissociation rates, lifetimes and widths obtained by this approximate calculation are summarized in Table 3.

3. Discussion

Since the adiabatic radial coupling is large, the results of the application of the Golden Rule to the

Table 3

Predissociation rates, lifetimes, widths and energies of three vibrational levels computed in both the diabatic and the adiabatic representations with bound states minima those of the E and F $^2\Pi$ states, respectively

Vib. level	Transition rate (T s^{-1})	Lifetimes (fs)	Widths (cm^{-1})	Vib. energy (cm^{-1})
Diabatic representation				
$v = 0$	0.6	1600	3	1253.8
$v = 1$	40	30	196	3795.5
$v = 2$	10	70	74	6342.5
Adiabatic representation				
$v = 0$	40	20	229	1550.5
$v = 1$	600	2	3337	3429.1
$v = 2$	100	9	611	5620.1

adiabatic representation can only give an 'order of magnitude' accuracy. Thus, from Table 3 it is evident that an excitation to any vibrational level of the F state leads to a fast dissociation the lifetime of such a level being in the fs range. That is, the state does not really exist. These lifetimes agree more or less with a previous estimate where excitations to the H $^2\Pi$ state had also been considered [6].

In the diabatic representation the radial interaction is small, and the Golden Rule is within its range of applicability. From Table 3 it is evident that only the $v = 0$ level has an appreciably long lifetime of the order of 2 ps. This long lifetime can be viewed as due to the weak interaction between the diabatic states, which increases the probability of the system remaining in the $v = 0$ level of the 'bound' diabatic state. This result agrees well with the recent experimental measurements of rotationally resolved predissociation lifetimes of the $v = 0$ level of the E $^2\Pi$ state [5], which range from 2.8 to 0.8 ps as the rotational levels change from $N' = 2$ to $N' = 15$ (our E state is denoted as D in Ref. [5]).

An attempt was made to 'predict' the experimental widths using a barrier penetration model [5]. However, to obtain a reasonable agreement with the experiment, the barrier height had to be raised by about 2200 cm^{-1} above the value obtained by a recent very accurate calculation [1]. This was probably due to the use of a model where the approximations employed were more appropriate to a narrow resonance than to a broad level close to the barrier top, as is the case here.

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