

# Dynamic Couplings, Radiative and Nonradiative Lifetimes of the $A^1\Sigma^+$ and $C^1\Sigma^+$ States of the KH Molecule

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# Dynamic Couplings, Radiative and Nonradiative Lifetimes of the $A^1\Sigma^+$ and $C^1\Sigma^+$ States of the KH Molecule

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In this article, dynamic couplings for X-A, X-C, and A-C, by using first and second derivatives terms neglected in the Born–Oppenheimer approximation, are calculated. Newly calculated radiative transition probabilities for the  $A^1\Sigma^+ \rightarrow X^1\Sigma^+$  and  $C^1\Sigma^+ \rightarrow X^1\Sigma^+$  emission bands of KH are used to calculate the radiative and nonradiative lifetimes of the various vibrational levels ( $0 \leq v \leq 35$ ) and ( $0 \leq v \leq 55$ ) of  $A^1\Sigma^+$  and  $C^1\Sigma^+$  states of the diatomic potassium hydride, KH, molecule. For higher vibrational levels, an estimate of the bound-to-free emission probability is also needed and included. Accurate positions, radiative and nonradiative lifetimes of states belonging to the adiabatic A and C states of the KH molecule are estimated. The results come from a Fermi's Golden Rule treatment in coupling calculation. That confirms the accuracy reached in both approaches and also in the treatment of the diabatic-adiabatic transformation. It involves, in particular, an effective phase choice that is needed to properly estimate nonadiabatic couplings. © 2007 American Institute of Physics. [DOI: 10.1063/1.2432887]

Key words: Born–Oppenheimer approximation; nonradiative lifetimes; radiative lifetimes; vibrational levels.

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## 1. Introduction

Accurate calculations of spectral profiles are an important tool in carrying out detailed comparisons between theoretical results and experimental data, thus allowing physical insight into molecular systems. For isolated transitions, as is the case here for the X, A, and C states of KH ( $X \rightarrow A$ ,  $X \rightarrow C$ , and  $A \rightarrow C$  transitions). We have simple Lorentzian profiles gov-

erned by radiative and nonradiative dissociation processes. The alkali hydrides ( $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ ) transition has been studied long ago by conventional spectroscopy and is now studied by dye laser excitation. The  $A^1\Sigma^+$  radiative lifetime has been measured for a few  $v'$  states in LiH (Refs. 1 and 2) and NaH.<sup>1,3</sup> In LiH, these radiative lifetimes have been calculated for all the  $v$  levels.<sup>4</sup> They show a maximum for intermediate  $v$  values and tend to the metal atom lifetime at the dissociation limit. Nonradiative lifetimes for LiH in the A state, using adiabatic and diabatic schemes, were estimated.<sup>5</sup> In these molecules, due to the relative location of  $X^1\Sigma^+$  and  $A^1\Sigma^+$  potential curves, it is possible to excite many  $A^1\Sigma^+v'$  states from  $X^1\Sigma^+v=0$  or 1 states, which are the most populated.

Experimentally, Marc *et al.*<sup>6</sup> have chosen the KH molecule as it is relatively easy to be produced in a discharge and to be excited by visible light obtained with common pulsed lasers. Radiative lifetimes,  $\tau$ , are measured in a series of  $A^1\Sigma^+v'$  states as completely as possible in order to look for a possible variation of  $\tau$  with  $v'$  (Giroud and Nedelec<sup>6</sup>). A difficulty in the theoretical calculation is that this radiationless process obviously violates the usual Born–Oppenheimer approach and evaluation of matrix elements of nuclear momentum operators is needed. Within the approximation, the bound vibration levels of the  $A^1\Sigma^+$  and  $C^1\Sigma^+$  states have an infinite nonradiative lifetime.

The actual finite nonradiative lifetime can be estimated within the adiabatic scheme from a golden rule approach involving the dynamic coupling with the continuum of the ground state  $X^1\Sigma^+$ . In a previous study,<sup>7</sup> we have determined nearly all adiabatic and diabatic  $^1\Sigma^+$  states below the ionic limit. This study has been recently extended to calculate dipole moments and to enlarge the range of internuclear distances. Taking advantage of a diabatic representation, we determine here in both adiabatic and diabatic schemes nonradiative lifetimes for all the vibrational levels of the  $A^1\Sigma^+$  and  $C^1\Sigma^+$  states of the KH molecule.

In the adiabatic scheme, the resonances of the A and C states appear well separated. Their associated widths are expected to be rather narrow due to the large energy difference with the  $X^1\Sigma^+$  state. Hence, a Fermi's Golden Rule to calculate nonradiative lifetimes should be reliable. Using this approximation, we have evaluated in the present work the full dynamic couplings including first and second derivatives, in contrast with the theoretical works done on LiH molecule, which is the simplest heteroatomic molecule,<sup>8</sup> where only the radial coupling has been taken in to account.

A practical numerical difficulty arises from the phase factors. Since the adiabatic states result from independent diagonalizations, they may change phase from one internuclear distance to the next. However, the integration over the whole internuclear range, where vibrational wave functions are nonvanishing, requires that the coupling does not change sign arbitrarily. When only two states are involved, this problem can easily be solved,<sup>9</sup> but we are dealing here with a manifold of nine states and have had to implement an original “phase fixer” algorithm. Using now the nine diabatic states, eight neutrals K (4s, 4p, 3d, 5s, 5p, 4d, 6s, and 4f) H

and one ionic  $K^+H^-$ , the resonances are very narrow, a very accurate guess is required for the positions, which should be within the narrow widths.

This article is organized as follows. Section 2 is devoted to the Golden Rule calculations, the main features of adiabatic and diabatic ab-initio calculations being also included there. In Sec. 3 we present the results with comparisons to experimental and theoretical recent works. Finally, some conclusions are outlined in Sec. 4.

## 2. Golden Rule Calculation in the Adiabatic Representation

In the adiabatic representation, for each internuclear distance,  $R$ , a set of  $n$  eigenvectors of the electronic Hamiltonian ( $\psi_i; i=1, n$ ) is used. The corresponding eigenvalues define the usual adiabatic potential energy curves ( $E_i; i=1, n$ ) for the nuclear motion. The solution of the vibrational equation

$$[T + E_i(R)]\chi_{i\vartheta} = E_{i\vartheta}\chi_{i\vartheta}, \quad (1)$$

where  $T = -(1/2\mu)(\partial^2/\partial R^2)$  is the nuclear kinetic energy operator in the non-rotating diatomic approximation, leads to a discrete spectrum ( $E_{i\vartheta}, \chi_{i\vartheta}$ ) and to a continuum one ( $E, \chi_{iE}$ ). Beyond the Born–Oppenheimer approximation, we have to evaluate dynamic couplings between the adiabatic states. There are two kinds of terms

$$f_{ij}(R) = \left\langle \psi_i \left| \frac{\partial}{\partial R} \right| \psi_j \right\rangle, \quad (2)$$

and

$$h_{ij}(R) = \left\langle \psi_i \left| \frac{\partial^2}{\partial R^2} \right| \psi_j \right\rangle. \quad (3)$$

Only  $h$  results in nonvanishing diagonal elements, which contribute to the adiabatic correction leading to new potentials

$$E_i^{\text{ac}}(R) = E_i(R) - \frac{1}{2\mu} h_{ii}(R). \quad (4)$$

And therefore to new discrete ( $E_{i\vartheta}^{\text{ac}}, \chi_{i\vartheta}^{\text{ac}}$ ) and spectra of continuum ( $E, \chi_{iE}^{\text{ac}}$ ), when a bound level of state  $j$  is resonant with a continuum level of state  $i$ , the bound state has a finite nonradiative lifetime which can be estimated using Fermi's Golden Rule ( $\hbar=1$ ),

$$\Gamma_{i \leftarrow j} = 2\pi \hbar |\langle \chi_{iE} | W_{ij} | \chi_j \rangle|^2, \quad (5)$$

$$\tau_{i \leftarrow j} = \frac{1}{\Gamma_{i \leftarrow j}}, \quad (6)$$

where  $W$  is the full dynamic coupling

$$W_{ij} = -1/2\mu[(h_{ij}(R) + 2f_{ij}(R)(\partial/\partial R))] \quad (7)$$

It can be easily shown that the integral appearing in Eq. (5) is symmetric in  $i$  and  $j$  even though the derivative operator acts in one case on the bound vibrational wave function and in

the other case on the continuum one. We will use the residual difference between  $W_{ij}$  and  $W_{ji}$  as a test of the numerical accuracy of the calculation. For the evaluation of  $\Gamma$ ,  $h_{ij}$  is often neglected without further justification; the expression is then no longer symmetric with respect to  $i \leftrightarrow j$  permutation. Taking advantage of the diabatic representation ( $\varphi_i; i=1, n$ ) where  $f_{ij}$  vanish, dynamic couplings can be easily evaluated. The two representations are related by an  $R$  dependent unitary transformation

$$\varphi_j = \sum_i U_{ij}^+(R) \psi_j, \quad (8)$$

$$(U^+ U = I). \quad (9)$$

We used a Hellmann–Feynman expression to evaluate  $f$ ,

$$f_{ij}(R) = \frac{1}{E_j(R) - E_i(R)} \left[ U(R) \frac{\partial V}{\partial R} U^+(R) \right]_{ij}, \quad (10)$$

where  $V$  is the electronic Hamiltonian in the adiabatic basis set (now diagonal). The diabatic potentials as well as their coupling vary smoothly and their derivatives do not present discontinuities. In turn,  $h$  can readily be obtained from  $f$  using the closure-relation

$$I_{mn} \approx \sum_{i=1}^n |\varphi_i \langle \varphi_i| \quad (11)$$

$$\text{leading to } h_{ij} = f_{ij}^2 + \frac{\partial f_{ij}}{\partial R}. \quad (12)$$

Since the matrix  $f$  is antisymmetric ( $f_{ij} = -f_{ji}$ ), all the diagonal elements of  $f_{ij}^2$  are negative and will lead to a positive contribution to the adiabatic correction. In many studies, the calculation of  $f$  using relation (10) has been compared to direct *ab initio* estimates. The comparison is fairly good, which clearly shows that the residual radial coupling between the diabatic states is extremely small and validates the diabaticization procedure used. In addition, the physical origin of the peaks in the radial coupling is clarified by a correlation with the crossings between the diabatic curves. This study<sup>10</sup> has confirmed the known neutral-ionic crossings and revealed unexpected neutral-neutral ones at short distances.

### 2.1. Phases

Since  $f$  and its derivative enter in the integral (5) over  $R$ , it is necessary that the matrix elements do not change phase from one point to another. Here again, we take advantage of the diabatic representation where by construction the diabatic states do have a global phase, the same for all internuclear distances. For any  $R$  value we have

$$\psi_i = \sum_j U_{ji}(R) \varphi_j. \quad (13)$$

We want to insure a global phase factor for the  $\psi$  vectors as defined by the columns of the matrix  $U$ . We notice that since  $R$  is here a parameter, all quantities related to  $U$  should behave smoothly as a function of this parameter. In particular, the determinant of  $U$  should not present any discontinuity



and remain constant since its value can be only 1 or  $-1$ . Keeping this argument in mind, we return to the 2 by 2 unitary transformation, which can be expressed analytically, and consider an avoid crossing. Going through it, a useful criterion to avoid any change of sign of the determinant is to impose, at consecutive points  $R_1$  and  $R_2$  the following requirement

$$\langle \psi_i(R_1) | \psi_i(R_2) \rangle = \sum_j U_{ij}^+(R_1) U_{ij}(R_2) 0. \quad (14)$$

The adiabatic vectors are ordered according to their energy, independently of their intrinsic characteristics, and this overlap can be small. In particular, if the two points are on different sides of an avoided crossing and, in addition, if the crossing is only weakly avoided, the overlap can be arbitrarily small. Indeed, as long as this overlap does not vanish, the criterion is effective in fixing the phase of the two vectors at point  $R_2$ . For the general case with  $n$  larger than two ( $n=9$  in the present study), we have adopted the same criterion and demonstrated that it remains successful. An alternative could have been to follow the largest component of the adiabatic vectors, but such an approach leads to severe difficulties when going through an avoid crossing.

## 2.2. Extrapolation to Short Distances

We have used a pseudopotential for the potassium core, which precludes confidence in *ab initio* calculations for very short internuclear distances where the hydrogen atom is penetrating into the core. Extrapolation of the repulsive wall is, however, required in order to account for the exponential decay of the vibrational wave functions at short internuclear distance. Extrapolation of the adiabatic energies is straightforward by resorting to a usual analytic expression  $A \exp(-BR)/R$  and fitting the parameters  $A$  and  $B$  to reproduce the *ab initio* results at the two shortest distances calculated ( $R=2.2$  and  $2.45$  a.u.). The extrapolation of the unitary transformation  $U$  for the diabatic representation requires smoothly matching  $U$  to the unit matrix  $I$ . The procedure is as follows. At  $R_0$  ( $=2.45$  a.u. here) we know  $U_0$ , for  $R < R_0$  we define the matrix  $M$ ,

$$M = f(R)U_0 + [1 - f(R)]I, \quad (15)$$

where  $f(R)$  is a Gaussian function centered at  $R_0$ , where  $f=1$  at  $R=R_0$ , and the results are almost insensitive to the remaining parameter. From  $M$ , using an orthogonal symmetric transformation, a unitary matrix  $U$  is constructed

$$U = M(M^\dagger M)^{-\frac{1}{2}} \quad (16)$$

and the extrapolated  $V$  matrix is given by

$$V = U^\dagger E U, \quad (17)$$

where  $E$  is the diagonal matrix of the extrapolated adiabatic energies. The objective of this extrapolation procedure is to ensure reasonable adiabatic energies and consistency with the diabatic picture. The width we are looking for are so small that any inconsistency leads to disagreement in the

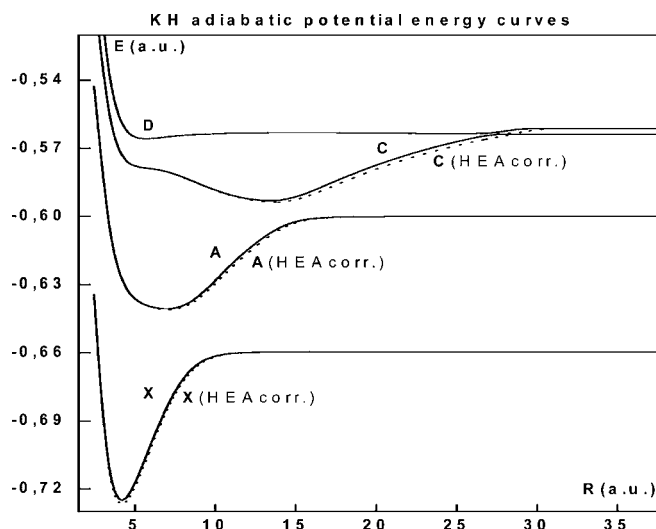


FIG. 1. KH adiabatic potential energy curves for  $1\Sigma^+$  states with and without the electron affinity correction of hydrogen.

final comparison between the adiabatic and diabatic approaches. Simpler procedures like direct extrapolation of the  $V_{ij}$  matrix elements have also been tested. They are less robust and subject to artifacts such as oscillations in the adiabatic energies.

## 3. Practical Implementation and Results

In practice, we have used the following procedure. For a grid of 150 interatomic distances ranging from 2.45 to 300 a.u. we determine by the *ab Initio* methods described by Boutalib *et al.*<sup>11</sup> and Gadea *et al.*,<sup>12,13</sup> the matrices  $V_{ij}(R_\alpha)$  ( $i, j=2,2; \alpha=1, 150$ ). For Each  $R_\alpha$  the  $V$  matrix is diagonalized defining the rotation matrix  $U(R_\alpha)$ . Extrapolation to short distances is performed and the phases are controlled. Dynamical two coupling elements  $f_{ij}$  and  $h_{ij}$  are computed according to Eqs. (10) and (12) and finally the non-radiative lifetimes are evaluated using the usual adiabatic potentials and also using the adiabatic corrections given by Eq. (4). We plot adiabatic and diabatic potential curves in Figs. 1 and 2.

The present calculations have been carried out taking into account correction for the hydrogen electron affinity. We have used an  $R$  dependent correction of the ionic diabatic curve, which accounts for basis set limitations. At short distances the potassium basis set increases the local completeness on the hydrogen atom and the error decreases with respect to asymptotic error. As can be seen in Ref. 7, a larger basis set for hydrogen could not be used because of numerical problems during the diabaticization process, the main effect of this rather small basis being an error ( $405 \text{ cm}^{-1}$ ) in the H electron affinity, which, however, is corrected due to diabatic approach used.

### 3.1. Dynamic Radial Coupling: $f_{ij}$ and $h_{ij}$

The resulting  $f_{ij}$  and  $h_{ij}$  are reported in Figs. 3–6 for the states  $i=X$  and  $j=A$  or  $C$  and  $i=A$  and  $j=C$ . There are no arbitrary changes of sign for either  $f$  or  $h$ . The  $h_{ij}$  term is not

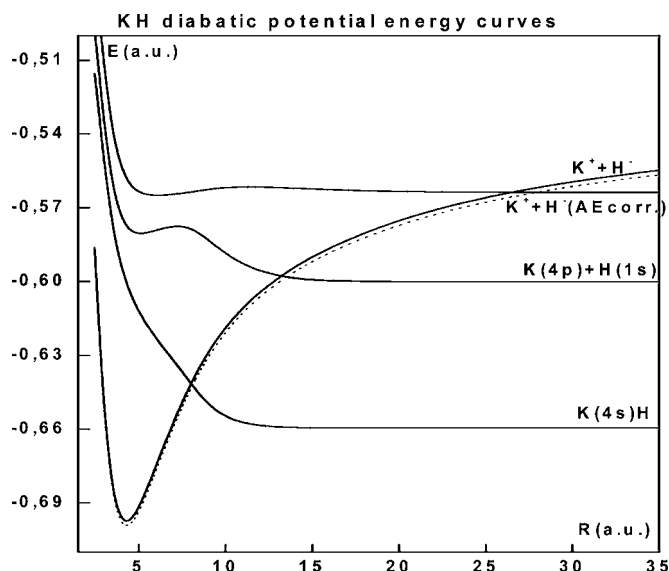


FIG. 2. KH diabatic potential energy curves for  $^1\Sigma^+$  states with and without the electron affinity correction of hydrogen.

vanishingly small and clearly cannot be neglected for the evaluation of the nonradiative lifetimes. For  $f_{ij}$ , X-A coupling is most significant because of the crossing avoided between the two corresponding states, X and A, which takes place at an internuclear distance of approximately 8.5 a.u. This curve presents a maximum and then tends towards zero at long distances. X-C coupling is weaker. It presents a significant variation at small distance and goes to zero at long distance. This is explained by the fact that the wave functions, when  $R$  increases, become increasingly atomic and their dependence on  $R$  decreases. At the asymptotic limit, the first derivative is equal to zero.

We note that the cases  $i-j=1$  are most significant. The corresponding curves go through zero each time the internuclear distance corresponds to an avoided crossing. The second derivative for the cases  $i-j>1$ , is not negligible. This requires, as for the  $f_{ij}$ , that a study based on this quantity, must take into account the entire system of coupled equations.

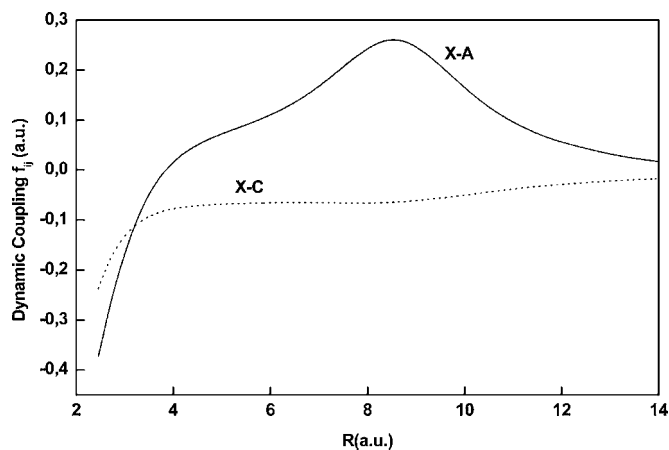


FIG. 3. Dynamic coupling  $f_{ij}$  for X-A (continuous line) and X-C (dashed line) of KH molecule.

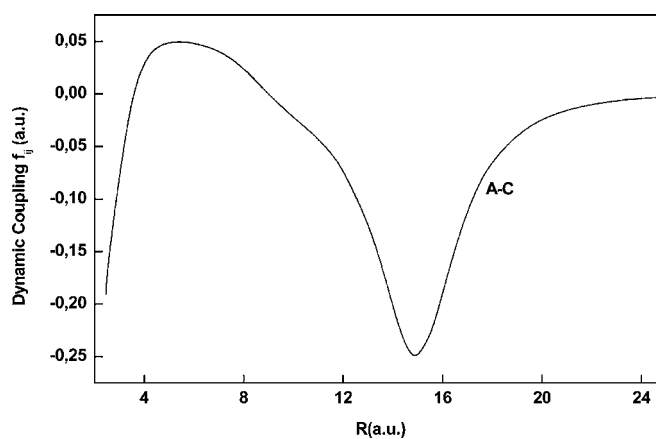


FIG. 4. Dynamic coupling  $f_{ij}$  for A-C of KH molecule.

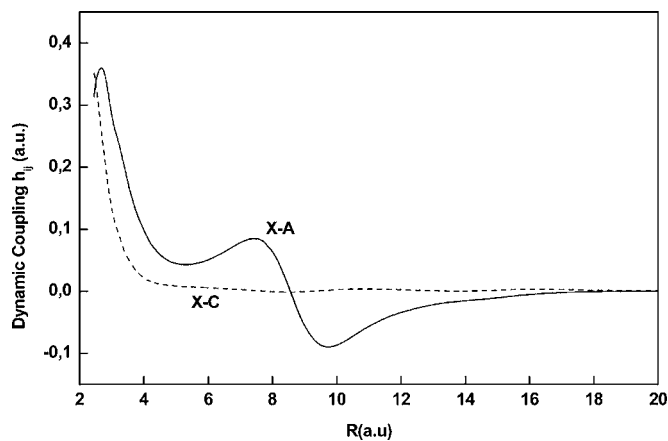


FIG. 5. Dynamic coupling  $h_{ij}$  for X-A (continuous line) and X-C (dashed line) of KH molecule.

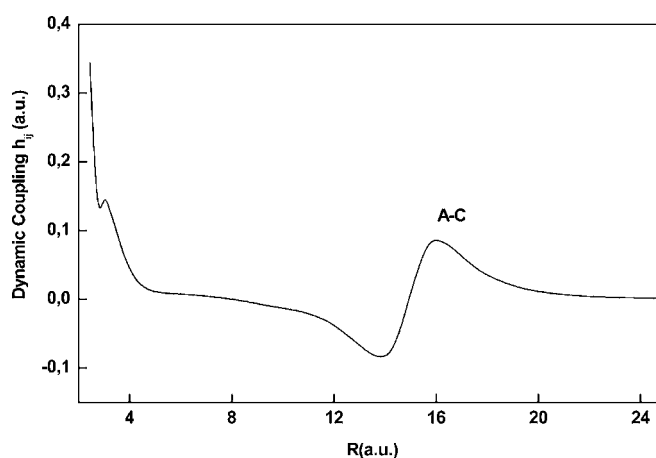


FIG. 6. Dynamic coupling  $h_{ij}$  for A-C of KH molecule.

### 3.2. Adiabatic Corrections

A rigorous *ab initio* calculation of this adiabatic correction is possible and was achieved.<sup>14</sup> It is then necessary to calculate the average values of this adiabatic correction for each electronic state considered. That is not our objective here. We only seek to consider the adiabatic corrections without returning to *ab initio* calculation, by simply exploiting knowledge of the electronic Hamiltonian in the diabatic and adiabatic representations.

The adiabatic correction rises from the use of the Born–Oppenheimer approximation. In this approximation, we assume that the particles are independent and that the movement of the electron and that of the core are completely uncoupled. This is based on the fact that the mass of the core is considerably larger than that of the electron; consequently we regard the total wave function as a simple product parametrically, of a nuclear wave function and electronic wave function, which depends on the internuclear distance,  $R$ .

The first theoretical calculation of the adiabatic correction was carried out in 1941 for the molecule  $H_2$ ,<sup>15</sup> a work followed by several others.<sup>16–26</sup> The hydrogen molecule was intensively studied by Kolos *et al.*<sup>25</sup> and Bishop.<sup>26</sup> For the heteronuclear molecules, the first molecule studied is  $HeH^+$ , a system made up of two electrons.<sup>24,27</sup> The study of the  $LiH$  molecule<sup>23–33</sup> is a logical continuation. It is more complex than  $HeH^+$ , but less complex than the others ( $NaH$ ,  $KH$ ,  $RbH$ , and  $CsH$ ...). During the theoretical calculation of the adiabatic correction, the main difficulty which arises, aside from the determination of the wave functions, is to develop methods of evaluating derivatives various choices of reference frames.

Yarkony *et al.* in the whole from their five articles<sup>31,34–37</sup> developed satisfactory techniques for evaluating derivatives. Handy *et al.*<sup>38</sup> observed that the method of evaluating derivatives in reference frame SFF allows an evaluation of the adiabatic correction. In the case of diatomic and triatomic molecules the passage towards the molecular reference frame (BFF) is of large a effectiveness,<sup>31,34–37</sup> especially when the wave functions are the result of a full interaction configuration.

The use of symmetry makes it possible to reduce the number of integrals to be calculated. Derivatives in our case are based on the rotation matrix, which ensures the transformation the adiabatic representation into the diabatic representation. For the second term, we apply the Viriel theorem of diatomic molecules. For the calculation of these two terms, we used *ab initio* results presented previously.<sup>7</sup> In next subsection, we present evaluation of the first and second terms of the adiabatic correction and their effects.

#### 3.2.1. Behavior of the First and the Second Terms of the Adiabatic Correction

The first term corresponds to the dynamic coupling  $h_{ij}$  (as calculated in Sec. 3.1 of this article). This correction is diagonal and positive. The fact that, this term is proportional to the integral of the  $h_{ij}$  term, results in a particular variation. It

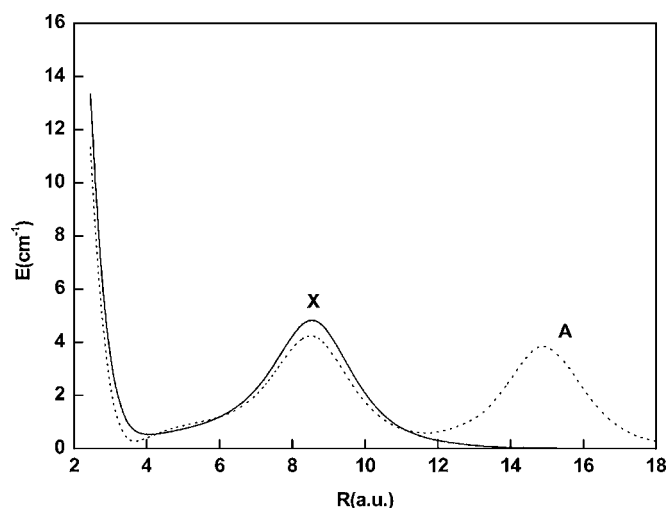


FIG. 7. First adiabatic correction term for the X and A states of KH molecule.

passes through a minimum on the level of the distance from equilibrium, then through maximum in the vicinity of the avoided crossing, and tends towards zero at long distance. This is explained by the fact that the electronic wave function at long distance no longer depends on internuclear distance. Figures 7 and 8 present successively the second adiabatic correction term for the pairs of states X and A, and C and D. The second adiabatic correction term is oscillatory. It is largest at short distance (about  $100\text{ cm}^{-1}$ ) and tends towards a constant value, at long distance, corresponding to the asymptotic electronic energy divided by the sum of the nuclear masses of the two atoms. Figures 9 and 10 present successively the second adiabatic correction term for the pairs of states X and A, and C and D.

#### 3.2.2. Influence of Adiabatic Correction on the Molecular Constants

We recomputed the molecular constants of the nine states by taking account of the first adiabatic correction term. The initial curves contain the correction in energy due to the electronic affinity. We note that generally the changes for the distance from equilibrium are about  $10^{-2}$ – $10^{-3}$ . But the correction is much larger for some states, where this correction changes the molecular constants significantly.

As can be seen in Table 1, for the depths of the wells the difference between the results with and without the first adiabatic correction term is only a few  $\text{cm}^{-1}$ , with the exception of some states, where it is about  $10\text{ cm}^{-1}$ . For example, the depth of the well of the D state (minimum at 5.65 a.u.) changes from 873.33 to 975.46  $\text{cm}^{-1}$ .

Refereed to Table 1, our results for the binding energy and the equilibrium distance are in good agreement with the experimental data,<sup>40</sup> being better than the previous results and comparable to the most recent one.<sup>39</sup> For higher excited states, no experimental data exist; our results are compared only with the most recent *ab initio* calculation.<sup>39</sup>

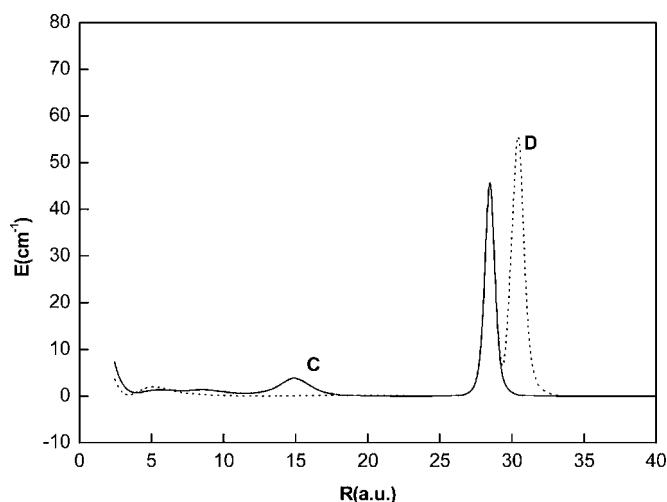


FIG. 8. First adiabatic correction term for the  $C$  and  $D$  states of KH molecule.

In Figs. 11 and 12, we present the displacement of the vibrational levels of  $X$  and  $A$  states of KH. This concerns the difference between energy of a level without and with the first adiabatic correction term. We note that this difference is positive and varies nonlinearly. This is explained by the fact that this first adiabatic correction term is positive: thus lifts the vibrational levels toward higher energy.

## 4. Radiative and Nonradiative Lifetimes

### 4.1. Radiative Lifetimes of the $A^1\Sigma^+$ and $C^1\Sigma^+$ States Due the Bound-Bound Contribution from the $X^1\Sigma^+$ State of KH

In this paragraph, we present the radiative lifetimes of the vibrational levels of the two electronic states  $A$  and  $C$ , the calculation of this important physical quantity, is carried out using Fermi's Golden Rule.

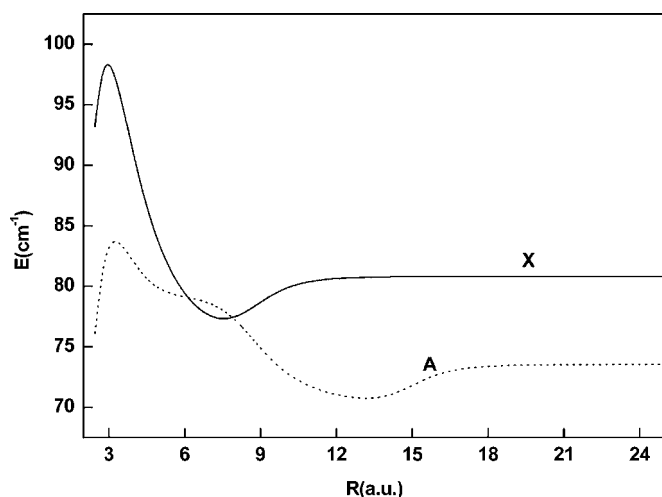


FIG. 9. Second adiabatic correction term for  $X$  and  $A$  states of KH molecule.

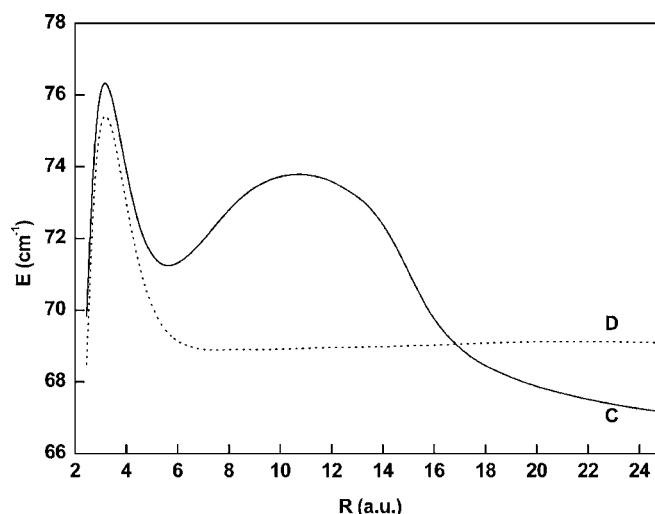


FIG. 10. Second adiabatic correction term for  $C$  and  $D$  states of KH molecule.

#### 4.1.1. Oscillator Strengths and Einstein's Coefficients

Specifying vibrational states  $n$  and  $m$ , the oscillator strength of the transition between these two states according to the Einstein coefficients is given by

$$f_{nm} = \frac{\mu_e h c^3 \bar{\nu}_{nm}}{\Pi e^2} B_{nm}, \quad (18)$$

where  $\mu$  and  $e$  are the mass and the charge of the electron,  $\bar{\nu}_{nm}$  is the wave number corresponding to the transition related to energy by the following formula:

$$\nu = \frac{E}{2\Pi \hbar c} = \frac{E}{hc}. \quad (19)$$

It is always possible to express the oscillator strength in terms of Einstein coefficients,  $A_{nm}$  and  $B_{nm}$ ,

$$A_{nm} = \frac{64\Pi^4 \bar{\nu}_{nm}^3 |D_{nm}|^2}{3hc^3} \quad \text{and} \quad B_{nm} = \frac{8\Pi^3 |D_{nm}|^2}{3h^2 c}, \quad (20)$$

where  $D_{nm} = \langle \Psi_n | D | \Psi_m \rangle$  is the electric dipole moment responsible for the transition between states  $n$  and  $m$ , which was calculated in previous work.<sup>7</sup> For a  $v'$  vibrational level of an electronic state ( $A$  or  $C$  for example), two possibilities

TABLE 1. Bond distances  $R_e$  (a.u.) and dissociation energies  $D_e$  (cm<sup>-1</sup>): (a) uncorrected results; (b) improved results including the first adiabatic correction term for the  $X$ ,  $A$ ,  $C$ , and  $D$  adiabatic states for the KH molecule.

		This work (a)	This work (b)	Lee <i>et al.</i> <sup>39</sup>	Stwalley <i>et al.</i> <sup>40</sup>
$X^1\Sigma^+$	$R_e$ (a.u.)	4.19	4.19	4.22	4.23
	$D_e$ (cm <sup>-1</sup> )	14750.41	14708.10	15066.6	14772.7
$A^1\Sigma^+$	$R_e$ (a.u.)	7.05	7.04	7.01	7.11
	$D_e$ (cm <sup>-1</sup> )	8946.27	8937.75	8811	8698
$C^1\Sigma^+$	$R_e$ (a.u.)	13.63	13.61	13.40	—
	$D_e$ (cm <sup>-1</sup> )	6584.50	6587.76	6516	—
$D^1\Sigma^+$	$R_e$ (a.u.)	5.65	5.65	5.59	—
	$D_e$ (cm <sup>-1</sup> )	873.33	975.46	881	—



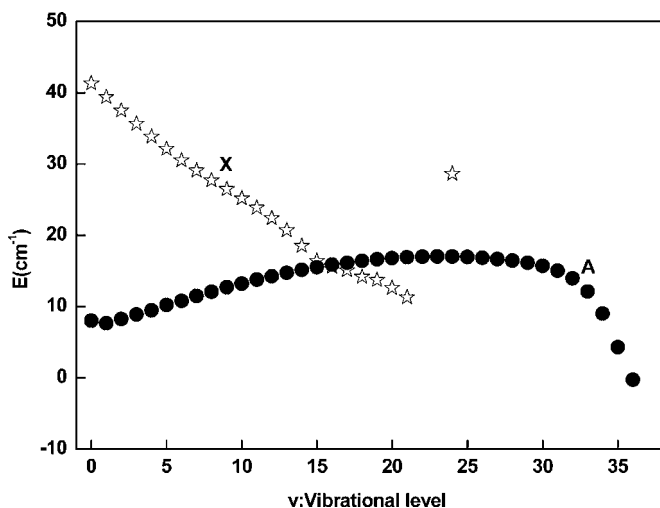


FIG. 11. Displacement of the vibrational levels of X and A states of KH molecule.

for emission exist. The first one corresponds to decay toward a vibrational level of a less excited electronic state, giving rise to a bound-bound transition. The second corresponds to emission toward a continuum, giving rise to a bound-free transition.

#### 4.1.2. Bound-Bound Transition

The radiative lifetime of a vibrational level  $v'$  for bound-bound transitions is given by

$$\tau_{v'} = \frac{1}{\Gamma_{v'}} \quad \text{and} \quad \Gamma_{v'} = \sum_{v=0}^{nvt} A_{vv'}, \quad (21)$$

where  $nvt$  is the total number of vibrational levels of the lower electronic state. In our calculation integrative  $R$  is carried out on a grid extending from 2.2 to 50 a.u. The values of the transition dipole moment for  $R$  between 2.2 and 2.45 a.u. are extrapolated by constant, which corresponds to the value of the transition dipole moment at 2.45 a.u.

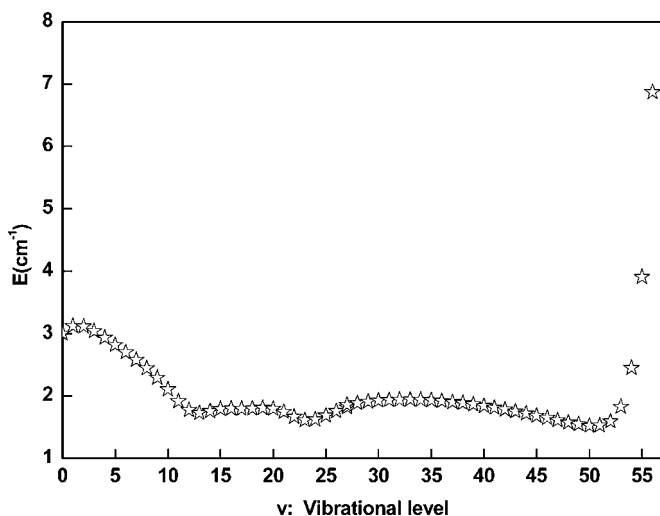


FIG. 12. Displacement of the vibrational levels of C state of KH molecule.

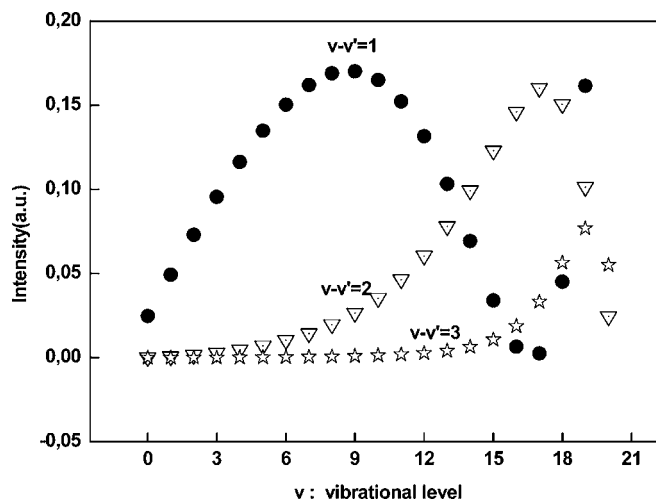


FIG. 13. Transitions between nonadjacent vibrational levels of the  $X^1\Sigma^+$  state of KH.

#### 4.1.3. Bound-Free Transition

The contribution to the radiative lifetime from transition toward the continuum is not negligible. It corresponds to transitions from one vibrational level  $v'$  toward all states in the continuum. The sum now becomes an integral, which we evaluate numerically. The radiative lifetimes corresponding to emission of a vibrational level  $v'$  toward the continuum of the lower electronic state are given by

$$\tau_{v'}(s) = \frac{1}{\Gamma_{v'}} \quad \text{and} \quad \Gamma_{v'}(s^{-1}) = 2.14198639 \times 10^{10} \int_{Eas}^E E^3 |\langle \chi_E | \mu | \chi_{v'} \rangle|^2 dE. \quad (22)$$

Here all the quantities used for calculation are in atomic units. The closure relation for a given electronic state composed of both discrete states (vibrational levels) and a continuum is written

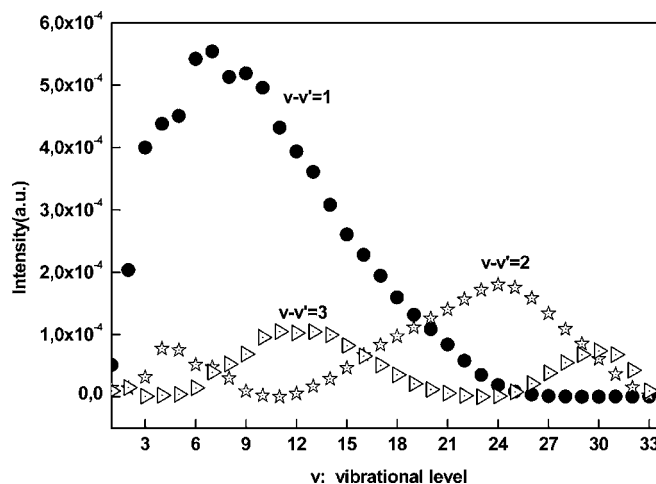


FIG. 14. Transitions between nonadjacent vibrational levels of the  $A^1\Sigma^+$  state of KH.

$$\sum_{\nu=0}^{n\nu} |\chi_{\nu}\rangle\langle\chi_{\nu}| + \int_{E_{as}}^{\infty} |\chi_E\rangle\langle\chi_E| dE = I. \quad (23)$$

The projection of an unspecified vibrational level noted  $|\chi_{\nu'}\rangle$  (belonging for example to a higher electronic state) gives us the integrated intensity of the continuum with this vibrational level

$$\int_{E_{as}}^{\infty} |\langle\chi_{\nu'}|\chi_E\rangle|^2 dE = 1 - \sum_{\nu=0}^{n\nu} |\langle\chi_{\nu'}|\chi_{\nu}\rangle|^2. \quad (24)$$

By using the approximation suggested by Zemke<sup>40</sup> the contribution to the lifetime due to the bound free transitions becomes

$$A_{\nu'}(\text{bound-free}) = cte |\mu(R_{\nu'+})|^2 FC_{\nu',\text{cont}}^{\nu_{\nu',\text{cont}}} \quad (25)$$

where  $\nu = E_{\nu'} - E_{as}$  is the difference in energy between the vibrational level and the asymptote of the lower electronic state.

$$FC_{\nu',\text{cont}} = 1 - \sum_{\nu=0}^{n\nu} |\langle\chi_{\nu'}|\chi_{\nu}\rangle|^2 \quad (26)$$

is the integrated Franck–Condon density of a vibrational level.

As can be seen in Table 2, our calculated radiative lifetimes of general vibrational levels of the A state of KH molecule, are in good agreement with the only experimental values, the difference is due to that in this experience, Giroud *et al.*,<sup>6</sup> use different values of rotational quantum number ( $J=8$  and  $J=9$ ), but in our calculation  $J=0$ .

Figures 15 and 16, present the radiative lifetimes of the vibrational levels of the two electronic states A and C, the calculation of this important physical quantity, is carried out using Fermi's golden rule.

## 4.2. Nonradiative Lifetimes of the $A^1\Sigma^+$ and $C^1\Sigma^+$ states of KH

These nonradiative contributions to the lifetime due to electronic predissociation, they correspond to an interaction between a vibrational level  $\nu'$  and the continuum having the same energy. The interaction is the radial coupling that result from the dynamic couplings  $f_{ij}$  and  $h_{ij}$ . These two quantities, which were calculated and presented in (Sec. 3.1) for X, A, and C states, are treated here like a perturbation of the Born–Oppenheimer Hamiltonian.

In this section, we present the nonradiative contributions to the lifetimes of the vibrational levels of the first two excited electronic states A and C. The line width is estimated by Fermi's Golden Rule, for a vibrational level  $\nu'$ , in interaction with the continuum having the same energy (the continuum in our case belongs to the electronic state X or A according to whether we study the vibrational levels of the A state or C state) is given by

$$\Gamma_{\nu'} = 2\pi |\langle\chi_{\nu'}|W_{12}|\chi_E\rangle|^2 \quad (27)$$

where the  $W_{12}$  operator is given by

TABLE 2. Radiative lifetimes of general vibrational levels of the  $A^1\Sigma^+$  state of the KH molecule with and without the electron affinity of hydrogen, in comparison with experimental data (in  $\mu\text{s}$ ). EA: electron affinity of hydrogen.

$\nu$	Without EA	With EA	Giroud <i>et al.</i> <sup>6</sup>
5	46.71	46.13	64
7	46.79	46.06	60
10	51.03	50.67	58
13	59.85	58.33	56
17	67.58	65.43	54
19	71.36	67.62	53
22	80.36	72.80	34

$$W_{12} = \frac{1}{2\mu} \left[ 2\langle\psi_2|\frac{d}{dR}|\psi_1\rangle\frac{d}{dR} + \langle\psi_2|\frac{d^2}{dR^2}|\psi_1\rangle \right] \quad (28)$$

and  $|\chi_{\nu}\rangle$  is the wave function of a vibrational level belonging to the A or C state. In the literature, often, only the first term is taken into account for the calculation of the nonradiative decay rates. In our case, we noted that the contribution from the second derivative (dynamic coupling  $h_{ij}$ ) is not negligible compared to those from the first derivative (dynamic coupling  $f_{ij}$ ). We will present here the decay rates of the vibrational levels of the A and C excited electronic states, by taking account or not of the electron affinity correction of hydrogen. We will illustrate also the effect of adding of the first adiabatic correction term to the potential curves on the result.

### 4.2.1. Nonradiative Lifetimes of the $A^1\Sigma^+$ State

Table 3 presents the nonradiative decay rates of the A state, without taking account of the correction of the electron affinity of hydrogen (second column), by taking account of the first adiabatic correction term but without the correction

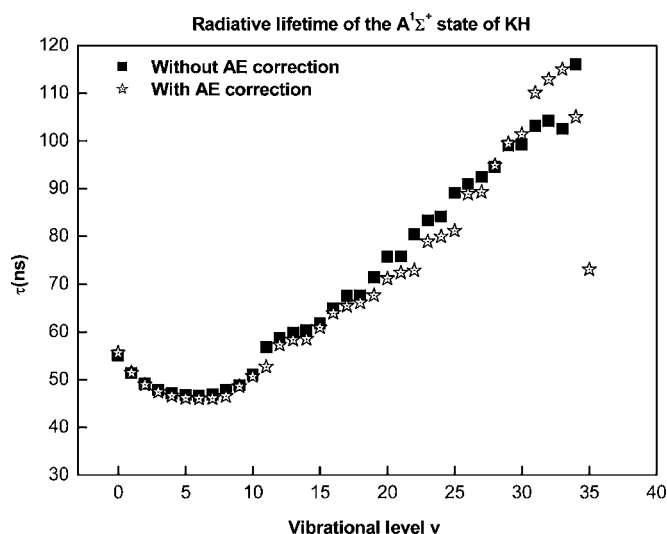


FIG. 15. Radiative lifetimes of the various vibrational levels of the  $A^1\Sigma^+$  state of KH with and without the electron affinity of hydrogen. Only the bound  $\rightarrow$  bound transition makes a significant contribution to these excited state (in ns).

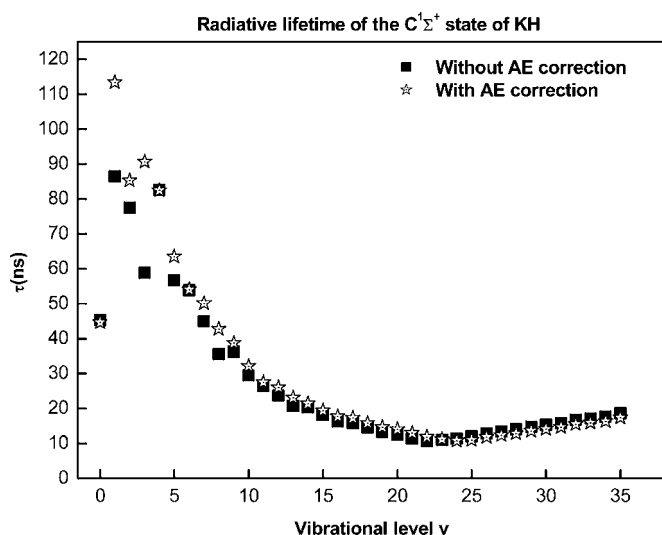


FIG. 16. Radiative lifetimes of the various vibrational levels of the  $C^1\Sigma^+$  state of KH with and without the electron affinity of hydrogen. Only the bound  $\rightarrow$  bound transition makes a significant contribution to these excited state (in ns).

of the electron affinity of hydrogen then by taking account of this electron affinity correction only and finally by taking account of both corrections. We observe that the nonradiative decay rate is smaller than the radiative decay rate. Consequently the total lifetime of a vibrational level is almost equal to the radiative lifetime.

#### 4.2.2. Nonradiative Lifetimes of the $C^1\Sigma^+$ State

For the  $C$  state, there are two contributions to the total nonradiative lifetime, the first corresponds to the coupling with the continuum of the  $A$  state and the second with that of the  $X$  state. We display in Table 4 the two contributions and their sum. The curves used in the calculation contain neither the correction in energy of the electron affinity of hydrogen nor the first adiabatic correction term.

Columns 2, 3, and 4 correspond respectively to the contribution due to the coupling with the continuum of state  $A$ , the coupling with the continuum of state  $X$  and finally their sum: total nonradiative lifetime. This result must be related to the kinetic energy of the continua and thus to the oscillations of the corresponding wave functions. The wave function of the  $X$  state continuum, degenerate with the vibrational level of the  $C$  state, for which we evaluate the nonradiative lifetime has a kinetic energy much larger than that of the  $A$  state, it thus oscillates much more rapidly and its integral with the bound level is smaller.

Moreover, the coupling operator (here radial coupling) has a maximum near the avoided crossing between the  $A$  and the  $C$  states. Thus the two factors contribute to a dominant contribution from the  $A$  state compared to that from the  $X$  state, for the nonradiative lifetime of the vibrational levels of the  $C$  state. Table 5, provides the total nonradiative lifetimes of the vibrational levels of the  $C$  state.

Columns 1, 2, 3, and 4, respectively display the results without any correction, without the electron affinity correc-

TABLE 3. Nonradiative lifetimes of the  $A^1\Sigma^+$  state of KH molecule (in  $\mu$ s). AC: Adiabatic correction. EA: electron affinity of hydrogen.

$v$	Without EA and without AC	Without EA and with AC	With EA and without AC	With EA and with AC
0	82.6402	83.30119	39.49524	39.25406
1	60.83308	61.82652	11.66893	11.78971
2	336.7466	340.18964	27.50626	28.09152
3	631.06965	701.74266	43.56846	43.86197
4	174.36869	162.36411	8.0919	8.27703
5	4.64766	4.62915	193.27927	225.97651
6	1.67011	1.68227	2.92791	2.9049
7	2.58149	2.62874	0.85896	0.86426
8	32.30602	30.39617	0.92643	0.94183
9	0.69486	0.69344	49.31893	56.88334
10	0.24449	0.24572	0.60212	0.5965
11	0.2294	0.23181	0.13645	0.13655
12	0.64245	0.65608	0.08442	0.08489
13	10.5543	9.83567	0.10747	0.10857
14	0.2275	0.22655	0.4772	0.48881
15	0.08008	0.08028	1.18671	1.15086
16	0.06099	0.06141	0.0821	0.08182
17	0.08413	0.08517	0.033	0.03305
18	0.35035	0.36055	0.02449	0.0246
19	1.30979	1.24345	0.02814	0.02837
20	0.07434	0.07362	0.05846	0.05928
21	0.02549	0.02541	0.70495	0.74194
22	0.01499	0.01499	0.1949	0.19012
23	0.01251	0.01253	0.03079	0.03054
24	0.01376	0.01382	0.01331	0.01326
25	0.02004	0.0202	0.0087	0.00869
26	0.04446	0.04516	0.00747	0.00748
27	0.27942	0.29268	0.00794	0.00796
28	1.03306	0.94495	0.01019	0.01025

tion of hydrogen but with the adiabatic correction (first correction term), with the electron affinity correction of hydrogen, and finally with the two corrections. At first, we note, although these corrections (the electron affinity of hydrogen and adiabatic correction) are small compared to the potential energy, their influence on the results is notable. Indeed, these corrections change the location of the levels.

## 5. Conclusions

In this article, using diabatic and adiabatic representations, while exploiting the adiabatic and diabatic potential curves of all  $^1\Sigma^+$  states below the ionic limit  $K^+H^-$ , obtained by extrapolation at short distances, we have determined the dynamic couplings, adiabatic corrections (first and second terms), the influence of electron affinity correction of hydrogen and the first adiabatic correction term on the molecular constants (equilibrium internuclear distance, dissociation energy and displacements of vibrational levels spacing).

Finally, for the first time, radiative and nonradiative lifetimes for all the vibrational levels of the  $A^1\Sigma^+$  and  $C^1\Sigma^+$  states have been accurately determined. The very good agreement between the various approaches, despite their theory based on different coupling mechanisms, illustrates

TABLE 4. Contributions of  $X^1\Sigma^+$  and  $A^1\Sigma^+$  states to the total nonradiative lifetime of the vibrational levels of the  $C^1\Sigma^+$  state of KH molecule (in  $\mu\text{s}$ ).

$v$	Contribution of A state ( $\times 10^{-3}$ )	Contribution of X state ( $\times 10^{-6}$ )	Total contribution ( $\times 10^{-3}$ )
0	290.15	9.1371	290.15
1	172.35	0.8400	172.35
3	21.83	38.900	21.83
4	4.950	1.8896	4.95
5	3.480	8.3590	3.48
6	9.270	709.71	9.27
7	25.070	0.7583	25.07
8	1.360	0.2326	1.36
9	0.59	2.4785	0.59
10	0.71	0.0949	0.708
11	6.07	0.0530	6.07
12	1.51	0.0892	1.51
13	0.28	37.906	0.284
14	0.23	0.0455	0.227
15	0.8	0.1259	0.803
16	1.74	0.0093	1.74
17	0.17	0.0178	0.168
18	0.15	0.1099	0.151
19	2.76	0.0908	2.76
20	0.21	0.0097	0.208
21	0.12	0.0053	0.123
22	73.72	1.9158	73.72
23	0.1	0.0022	0.102
24	0.3	0.0031	0.303
25	0.24	0.0076	0.239
26	0.07	0.0006	0.072
27	0.45	0.0004	0.452
28	0.18	0.0006	0.184
29	0.05	0.0007	0.054
30	0.12	0.0006	0.122
31	1.76	0.0005	1.76
32	0.06	0.0006	0.063
33	0.04	0.0008	0.042
34	0.12	0.0009	0.116
35	2.75	0.0008	2.75

the accuracy of the present calculations and of Fermi's Golden Rule estimates. Small changes of the potentials due to the adiabatic correction have also been tested. They do not lead to import modifications of the nonradiative lifetimes which appear as robust estimates with methodological as well as numerical stability. However, the lifetimes exhibit large and rather erratic variations with vibrational levels.

In Table 1, selected molecular constants are compared with previous results and one can see the improvement obtained from the use of the adiabatic correction and the electron affinity of hydrogen atom. The theoretical work of Lee *et al.*<sup>39</sup> used a full-calculation which took much time. In this work, we have used a molecular system composed of the hydrogen atom in interaction with a core of potassium and its two valence electrons; the calculation is very quick and yields results similar to experimental data.<sup>40</sup>

Our theoretical study of the KH molecule suggests a very interesting experimental study that would be valuable;

TABLE 5. Nonradiative lifetimes of the vibrational levels of the  $C^1\Sigma^+$  state of KH (in  $\mu\text{s}$ ).

$v$	Without EA and without AC ( $\times 10^{-3}$ )	Without EA and with AC ( $\times 10^{-3}$ )	With EA and without AC ( $\times 10^{-3}$ )	With EA and with AC ( $\times 10^{-3}$ )
0	290.15	299.87	2348.01	2787.15
1	172.35	182.51	115.14	112.44
2	11033.59	7415.29	10.31	10.43
3	21.83	21.77	4.14	4.24
4	4.95	5.02	5.63	5.87
5	3.48	3.56	2854.65	8028.09
6	9.27	9.67	2.23	2.21
7	25.07	23.95	0.592	0.596
8	1.36	1.36	0.443	0.45
9	0.59	0.595	0.989	1.02
10	0.708	0.718	36.48	32.63
11	6.07	6.32	0.403	0.402
12	1.51	1.5	0.154	0.155
13	0.284	0.285	0.167	0.169
14	0.227	0.229	0.883	0.903
15	0.803	0.816	0.764	0.756
16	1.74	1.72	0.104	0.105
17	0.168	0.169	0.079	0.079
18	0.151	0.152	0.281	0.285
19	2.76	2.83	0.606	0.6
20	0.208	0.208	0.065	0.065
21	0.123	0.123	0.077	0.078
22	73.72	70.7	21.02	19.94
23	0.102	0.103	0.06	0.06
24	0.303	0.304	0.118	0.118
25	0.239	0.239	0.175	0.176
26	0.072	0.072	0.043	0.043
27	0.452	0.456	0.453	0.456
28	0.184	0.184	0.075	0.075
29	0.054	0.055	0.034	0.034
30	0.122	0.123	0.171	0.172
31	1.76	1.74	0.137	0.137
32	0.063	0.063	0.028	0.028
33	0.042	0.043	0.036	0.036
34	0.116	0.117	0.701	0.71
35	2.75	2.69	0.074	0.074

namely, a calculation of the potential surfaces for Rydberg states of  $(\text{KH}_2)^*$ . The current development of lasers allows experimentalists to study the excited states of the alkali hydrides ( $\text{NaH}$ ,  $\text{CsH}$ ,  $\text{RbH}\dots$ ) and they may be particularly well suited to this task and in view of the total lack of theoretical dynamic information, the experimental results would be most welcome. We expect that the present contribution will encourage further experimental studies on this heteroatomic molecule.

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