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Nonradiative lifetimes for LiH in the A state using adiabatic and diabatic schemes

F. X. Gadéa and H. Berriche

Laboratoire de Physique Quantique, UMR 5626, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex, France

O. Roncero, P. Villarreal, and G. Delgado Barrio

Instituto de Matemáticas y Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain

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Accurate positions and nonradiative lifetimes of states belonging to the adiabatic A state of LiH are estimated. The results coming from a Golden Rule treatment in the adiabatic scheme present excellent agreement with those obtained through a diabatic close 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 control that is needed to properly estimate nonadiabatic couplings. Also, a powerful numerical procedure to obtain energy profiles in the diabatic close coupling frame is described and applied in this work. © 1997 American Institute of Physics. [S0021-9606(97)01048-9]

I. INTRODUCTION

Accurate calculation of spectral profiles is an important tool in carrying out detailed comparisons between theoretical results and experimental data allowing physical insight on molecular systems. For isolated transitions, as is the case here for the A state of LiH ($A \leftarrow X$ transition), we have simple Lorentzian profiles governed by radiative and nonradiative dissociation processes. Despite that LiH is the simplest heteroatomic molecule and a considerable experimental interest has been devoted to it (for a review see Ref. 1), only radiative lifetimes has been theoretically studied.^{2,3} Nonradiative lifetimes have been crudely estimated by Zemke *et al.*⁴ to be of the order of the microsecond, while a somewhat better estimation was given by Till *et al.*⁵ using an $X\alpha$ approach. However, this approach is doubtful here because of the neutral ionic crossing which imprints both the X and A states. Their large order of magnitude (μ s) as compared with radiative lifetimes (ns) made nonradiative lifetimes difficult to be measured. Therefore, the actual knowledge on this basic dissociative process only relies on approximate theoretical estimations. We present here a realistic study for all the vibrational levels of the A state of the ^7LiH .

A difficulty in the theoretical calculation is that this radiationless process obviously breaks the usual Born-Oppenheimer (BO) approach and evaluation of matrix elements of nuclear momentum operators are needed. Within the BO approximation, the bound vibrational levels of the A state 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. Another approach, based on a close coupling vibronic approach, can be implemented using a diabatic representation involving only potential couplings within a manifold of electronic diabatic states.

In a previous study⁶ we have determined nearly all adiabatic and diabatic $^1\Sigma$ states below the ionic limit. This study

has been recently extended to calculate dipole moments⁷ 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 state. Since the two approaches use completely different coupling operators, agreement between them emphasizes the accuracy of the calculation. In the adiabatic scheme, the resonances of the A state appear well separated and their associated widths are expected to be rather narrow due to the large energy difference with the X state. Hence, a Fermi's Golden Rule to estimate 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 previously mentioned estimation where only the radial coupling has been taken into 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 another. However, the integration over the whole internuclear range, where vibrational wave functions are nonvanishing, requires that the coupling does not change arbitrary of sign. When only two states are involved, this problem can be easily solved,⁸ but we are dealing here with a manifold of eight states and have had to implement an original "phase fixer" algorithm.

Using now the eight diabatic states, seven neutrals $\text{Li}(2s,2p,3s,3p,3d,4s,4p)\text{H}$ and one ionic Li^+H^- , a close coupling calculation presents two main difficulties. Since the resonances are very narrow we need a very accurate guess for the positions which should be within the narrow widths. To realize the difficulty, suffice to recall that a lifetime of $1\ \mu\text{s}$ means a width of $5.3 \times 10^{-6}\ \text{cm}^{-1}$. According to the Fano's theory, the width is related to the Lorentzian line-shape of the amplitude of the bound part of the vibrational wave function. In order to save storage, this amplitude is

here evaluated using a direct method within a propagation formalism.

The paper is organized as follows. Section II is devoted to the Golden Rule calculations, the main features of adiabatic and diabatic *ab initio* calculations being also included there. In Section III we present the approach developed for the close coupling calculation using the diabatic representation and compare the results. Finally, some conclusions are outlined in Section IV.

II. 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 (ψ_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 resolution of the vibrational equation

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

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

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

and

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

Only h presents 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 ($E_{iv}^{\text{ac}}, \chi_{iv}^{\text{ac}}$) and continuum (E, χ_{iE}^{ac}) spectra. 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 the Golden Rule

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

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

where W is the full dynamic coupling

$$W_{ij}(R) = -\frac{1}{2\mu} \left(h_{ij}(R) + 2f_{ij}(R) \frac{\partial}{\partial R} \right). \quad (7)$$

It can be easily shown that the integral appearing in Eq. (5) is symmetric in i and j despite 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 as a test of the numerical accuracy of the calculation.

For the evaluation of Γ , h_{ij} is often neglected without further justification; the expression is then no longer symmetric with respect to the $i \leftrightarrow j$ permutation.

Taking advantage of the diabatic representation (φ_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

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

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

We used an Hellmann-Feynman expression to evaluate f

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

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

$$I_{nn} \simeq \sum_{i=1}^n |\varphi_i\rangle \langle \varphi_i| \quad (11)$$

leading to

$$h_{ij} = (f^2)_{ij} + \frac{\partial f_{ij}}{\partial R}. \quad (12)$$

Since the matrix f is antisymmetric ($f_{ij} = -f_{ji}$), all the diagonal elements $(f^2)_{ii}$ are negative and will lead to a positive contribution to the adiabatic correction.

In a previous study, the calculation of f using relation (10) has been compared to direct *ab initio* estimations.⁹ 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 enlightened by a clear correlation with the crossings in the diabatic curves. This study¹⁰ has confirmed the known neutral-ionic crossings and revealed unexpected neutral-neutral ones at short distances.

A. Phases

Since f and its derivative enter in the integral (5) over R , it is necessary that the matrix elements do not change of 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. The problem can thus be restricted to the matrix U . 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 ψ 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 smooth as a function of this parameter. In particular,

the determinant of U should not present any discontinuity and remain constant since it can be only 1 or -1 . Keeping this argument in mind, we turn back to a 2 by 2 unitary transformation which can be written analytically and consider an avoided crossing. Going through it, a useful criterium to avoid any change of sign of the determinant is to impose at consecutive points R_1 and R_2 the following requirement:

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

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 the 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 criterium is effective in fixing the phase of the two vectors at point R_2 . For the general case with n larger than two ($n=8$ in the present study), we have adopted the same criterium and realized 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 troubles when going through an avoided crossing.

B. Extrapolation to short distances

We have used a pseudopotential for the lithium core which prevents confidence of *ab initio* calculations for very short distances where the hydrogen atom is penetrating into the core. Extrapolation of repulsive walls is, however, required in order to account for the inner exponential decay of the vibrational wave functions. 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 ($R=1.8$ and 2.0 a.u.). The extrapolation of the unitary transformation U for the diabatic representation requires a special attention. We used here a switching function which smoothly matches U to the unit matrix I . The procedure is as follows. At R_0 ($=1.8$ 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 $f=1$, and the results are almost not sensitive to the remaining parameter. From M , using an orthogonal symmetric transformation, a unitary matrix U is reached,

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

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 insure 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 final

FIG. 1. Potential energy curves for LiH $^1\Sigma$ states in the adiabatic representation with and without the correction for the electroaffinity of hydrogen.

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.

C. Practical implementation and results

In practice, we have used the following procedure. For a grid of 110 interatomic distances ranging from 1.8 to 243 a.u. we determine by the *ab initio* methods described in Refs. 6,11,12 the matrices $V_{ij}(R_\alpha)$ ($i, j=1,8; \alpha=1,110$). For each R_α the V matrix is diagonalized defining the rotation matrix $U(R_\alpha)$. Extrapolation to short distances is performed and the phases are controlled. Dynamical couplings f_{ij} and h_{ij} are computed according to equations (11) and (13) and finally the nonradiative lifetimes are evaluated using the usual adiabatic potentials and also using the adiabatic corrections given by equation (4).

We plot adiabatic and diabatic curves in Figures 1 and 2. The present calculations have been carried out taking into account a correction for the hydrogen electroaffinity. We used a R dependent correction of the ionic diabatic curve which accounts for basis set limitations. At short distances

FIG. 2. Potential energy curves for LiH $^1\Sigma$ states in the diabatic representation with and without the correction for the electroaffinity of hydrogen.

the lithium basis set increases the local completeness on the hydrogen atom and the error decreases with respect to the asymptotic error. In a preceding study we have shown that the results with and without the asymptotic correction brackets all the observed vibrational spacings for the A state. Thus, the main errors in the *ab initio* calculation come from basis set limitations for the determination of the hydrogen electroaffinity. As can be seen in Table VI of Ref. 6 the R dependent correction leads to realistic vibrational spacings in good agreement with the observed ones.

The resulting f_{ij} , h_{ij} , h_{ii} and h_{jj} are reported in Fig. 3 for the states $i=X$ and $j=A$. There is no arbitrary change of sign for either f or h . The contribution h_{ij} is not vanishingly small and clearly cannot be neglected for the evaluation of the nonradiative lifetimes. The peaks of h_{ii} and h_{jj} and the oscillations of h_{ij} near $R=2$ a.u. should be related to the high energy crossings between the neutral diabatic curves ($2s, 2p, \dots$).¹⁰

The results for the adiabatic approach are listed in Table I. As can be seen from the differences in evaluating W_{XA} or W_{AX} , the largest disagreements are of $\approx 10^{-8}$ s and so the present calculation of nonradiative lifetimes becomes highly accurate. Taking now into account adiabatic diagonal corrections leads to the results reported in Table II. The vibrational

FIG. 3. f_{ij} , h_{ij} , h_{ii} and h_{jj} for the states $i=X$ and $j=A$.

levels are shifted to higher energies since this contribution is positive by construction, but the lifetimes remain very similar to the previous ones and only a small difference can be noticed. Again, the difference between the calculations involving W_{XA} or W_{AX} are extremely small and in any way much smaller than the difference arising from the inclusion of adiabatic corrections.

Having now studied the stability of the results within the adiabatic scheme, it is interesting to notice that at this stage we have determined the position of vibrational levels only within a few wave numbers while their nonradiative width is estimated with an accuracy several orders of magnitude better $\approx 10^{-7}$ cm⁻¹. This is a nice advantage of the Golden Rule approximation. Methods like the close coupling approach developed in the next section, which directly determine the width from the profile are faced to the difficulty that the position should be determined with an accuracy similar to the width, that is particularly acute here where we have to deal with extremely small widths.

III. CLOSE COUPLING CALCULATION IN THE DIABATIC REPRESENTATION

Using now the diabatic representation, we have a manifold of eight states $\{\varphi_i\}$ which are only coupled by the electronic Hamiltonian. The continuum total wave function at energy E corresponding to the j open channel can be expanded as (incoming or outgoing character being considered)

TABLE I. Position (in cm^{-1} relative to the X asymptote) and nonradiative lifetimes (in microsecond) for the vibrational levels of the A state using the adiabatic representation. v : vibrational level, E^a : adiabatic Born-Oppenheimer energy, τ_{XA}^a : nonradiative lifetime using the coupling operator W_{XA} , τ_{AX}^a : as before using now W_{AX} .

v	E^a	τ_{XA}^a	τ_{AX}^a
0	6358.227	37.0253	37.0234
1	6637.557	6.1506	6.1502
2	6948.937	69.2767	69.2435
3	7282.841	15.7159	15.7112
4	7633.969	9.2685	9.2695
5	7998.020	10.1079	10.1045
6	8371.748	2.4466	2.4462
7	8752.649	4.3174	4.3165
8	9138.390	35.8141	35.8104
9	9526.951	6.7868	6.7842
10	9916.649	1.0389	1.0385
11	10305.877	0.4972	0.4971
12	10693.210	0.5155	0.5154
13	11077.309	1.0721	1.0718
14	11456.882	6.3649	6.3627
15	11830.638	84.9539	85.0009
16	12197.268	6.5636	6.5650
17	12555.373	18.1966	18.2058
18	12903.354	11.8331	11.8266
19	13239.274	0.9847	0.9845
20	13560.735	0.3475	0.3475
21	13864.668	0.2164	0.2164
22	14146.858	0.1917	0.1917
23	14401.257	0.1969	0.1969
24	14619.062	0.2736	0.2735
25	14787.092	0.4618	0.4617
26	14886.452	1.2876	1.2874

TABLE II. As Table I taking now into account the adiabatic corrections.

v	E^{ac}	τ_{XA}^{ac}	τ_{AX}^{ac}
0	6361.346	36.6495	36.6477
1	6640.808	6.1378	6.1373
2	6952.376	69.5322	69.4988
3	7286.396	15.7970	15.7923
4	7637.586	9.4109	9.4119
5	8001.645	9.9385	9.9353
6	8375.335	2.4442	2.4437
7	8756.170	4.3450	4.3440
8	9141.826	36.8813	36.8774
9	9530.292	6.7103	6.7077
10	9919.894	1.0369	1.0365
11	10309.030	0.4978	0.4977
12	10696.280	0.5167	0.5166
13	11080.308	1.0752	1.0750
14	11459.827	6.3922	6.3900
15	11833.547	84.4772	84.5237
16	12200.165	6.5641	6.5655
17	12558.283	18.1738	18.1830
18	12906.302	11.8786	11.8721
19	13242.286	0.9865	0.9864
20	13563.825	0.3481	0.3480
21	13867.827	0.2168	0.2167
22	14150.033	0.1921	0.1920
23	14404.312	0.1974	0.1974
24	14621.753	0.2747	0.2746
25	14789.053	0.4652	0.4651
26	14887.277	1.3159	1.3157

$$\Psi_E^{j(\pm)} = \sum_i^{n=8} \chi_{iE}^{j(\pm)}(R) \varphi_i. \quad (18)$$

After substitution in the Schrödinger equation, one arrives to the usual coupled equations for the nuclear motion

$$[T + V_{jj}(R) - E] \chi_{jE}^{j(\pm)}(R) = - \sum_{i \neq j} V_{ij}(R) \chi_{iE}^{j(\pm)}(R). \quad (19)$$

Above the lowest asymptote, which coincides with that of the adiabatic X state, all the vibrational states become resonances and their associated wave functions present both a bound and a continuum character. For well isolated resonances, and following Fano,¹³ the “exact” wave function in the neighborhood of a resonance l can be expressed as

$$\Psi_E^{j(\pm)} = a_j(E) \Psi_l^{\text{bound}} + \text{“continuum part”} \quad (20)$$

and then the square modulus of the bound amplitude

$$|a(E)|^2 = \sum_j |a_j(E)|^2 = \sum_j |\langle \Psi_l^{\text{bound}} | \Psi_E^{j(\pm)} \rangle|^2 \quad (21)$$

presents a Lorentzian profile as a function of the energy E . The width of this Lorentzian provides Γ , the inverse of the lifetime τ . A typical profile is depicted in Fig. 4 together with the calculated point in energy. The fit by a Lorentzian

function is almost perfect. We turn now to the determination of the grid in energy and to the calculation of the bound amplitude.

For very narrow resonances, whose widths are of the order of 10^{-6} cm^{-1} in this case, it is very difficult to locate their exact positions unless a good initial guess can be estimated. Due to adiabatic corrections, and more generally vibronic couplings and also the coupling with the continua, the resonance is shifted with respect to the adiabatic BO position. To determine accurately enough the position (E_l) of

FIG. 4. Lorentzian fit of $|a(E)|^2$ (arbitrary units) obtained through the diabatic close coupling scheme versus energy. $E=0$ corresponds to the estimated zero-order position of the resonance, close to the energy of the $v=11$ level in the adiabatic A state.

each resonance we have computed and diagonalized the Hamiltonian matrix as explained below. We evaluate the exact wave function and its bound amplitude at several energies around (E_i), A Lorentzian is then fitted to $|a(E_k)|^2$ to obtain the exact position and the width of this resonance.

A. Initial guess for the position of the resonances

To have a zero-order estimation of the position of the resonances, we look for discrete solutions of the Schrödinger equation

$$H\Psi_l = E_l\Psi_l. \quad (22)$$

This is done in the diabatic scheme by building up the matrix representation of the Hamiltonian, i.e., the vibronic matrix, in a given basis set and then diagonalizing it. By considering the product of vibrational ($\chi_\alpha, \alpha=1, N$) and electronic ($\varphi_i, i=1, n$) functions as basis set, the total wave function is then expanded as

$$\Psi_l = \sum_{i=1}^{n=8} \sum_{\alpha=1}^N A_{i\alpha}^l \chi_\alpha(R) \varphi_i \equiv \sum_{i=1}^{n=8} B_i(R) \varphi_i. \quad (23)$$

A block being related to a given electronic state, the kinetic operator is block-diagonal while the potential operator presents both block-diagonal and block-extradagonal terms

$$H_{i\alpha, j\beta} = \langle \chi_\alpha | \delta_{ij} T + V_{ij} | \chi_\beta \rangle. \quad (24)$$

For the vibrational basis set we have tested various approaches. The most reliable results have been obtained when using the eigenfunctions corresponding to the diabatic ionic curve ($V^{\text{lon}}(R)$), i.e., those satisfying the equation

$$\left[-\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + V^{\text{lon}}(R) \right] \chi_\alpha(R) = E_\alpha^{\text{lon}} \chi_\alpha(R). \quad (25)$$

They have been accurately determined by means of a Numerov algorithm over a grid of 20000 points. The reason for this choice is that its well spans the whole interesting energy

range and leads to bound states which also span the whole interesting R range. Using the diabatic representation it is not necessary to compute again the nuclear kinetic operator since we have

$$\langle \varphi_i \chi_\alpha | T | \varphi_j \chi_\beta \rangle = \delta_{ij} (E_\alpha^{\text{lon}} \delta_{\alpha\beta} + \langle \chi_\alpha | V_{ii}(R) - V^{\text{lon}}(R) | \chi_\beta \rangle). \quad (26)$$

In this way, only potential-like integrals have to be evaluated for the full vibronic approach.

Since these zero-order bound states are immersed in the continua, it is difficult to determine with a single diagonalization whether they correspond to resonances or to discretized continuum functions. Based on stabilization methods,¹⁴ the identification of actual zero-order bound states is performed by varying the number of vibrational functions in the basis set, from 100 to 120 in this case. So that only those eigenstates whose eigenvalues are almost unaffected by this change correspond to resonances or to real bound states of the system. A discrete variable representation, based on harmonic oscillators, have also been tested (with N about 300), leading to larger vibronic matrices. Moreover, the bound and quasibound states are some orders of magnitude worse stabilized than the previous approach.

B. Numerical calculation of $|a(E)|$

The numerical resolution of the coupled differential equations, Eq. (19), is done using the standard Fox-Numerov method¹⁵ in a radial grid composed by m equidistant points. In this method the ratio square matrix, defined as

$$\mathcal{R}(k-1) = \chi(k-1) \chi^{-1}(k) \quad (27)$$

is propagated from $k=2$ to m , being zero at $k=0$ to fulfill the regular boundary conditions at $R=0$. In the previous equation, $\chi(k)$ is the general $n \times n$ solution matrix of the coupled differential equations at R_k . Its columns with physical meaning, i.e., those for $j \leq \text{nop}$ (nop being the number of open dissociative channels) satisfy the boundary conditions,

$$\chi_i^j(R) \underset{R \rightarrow \infty}{\propto} \sqrt{\frac{2\mu}{\pi \hbar^2}} \begin{cases} \left[\delta_{ij} \frac{\sin k_j R}{\sqrt{k_j}} + \frac{\cos k_i R}{\sqrt{k_i}} K_{i,j} \right] & \text{for } i \leq \text{nop} \\ \frac{e^{k_i R}}{\sqrt{k_i}} E_{i-\text{nop}, j} & \text{for } \text{nop} < i < n \end{cases}. \quad (28)$$

Therefore, imposing the previous behavior for χ at the two last points of the radial grid and using the calculated $\mathcal{R}(m-1)$ matrix, the K and E matrices (of dimension $\text{nop} \times \text{nop}$ and $n - \text{nop} \times \text{nop}$, respectively) are obtained and also $\chi_{iE}^j(R_m)$. Thus, the entire wave function can be reconstructed using Eq. (27) as $\chi(k) = \Pi_{j=k}^{m-1} \mathcal{R}(j) \chi(m)$ in a second backward propagation.

The K matrix provides the transformation from these functions to the proper travelling ones through,

$$\chi^{(\pm)}(k) = \chi(k) (I \mp iK)^{-1}. \quad (29)$$

Within this numerical procedure the bound amplitudes of the exact wave function at a given energy E become,

$$a_j(E) = \sum_{i=1}^n \int dR B_i(R) \chi_i^{j(\pm)}(R) \approx \Delta \sum_i \sum_k B_i(R_k) \chi_i^{j(\pm)}(R_k) \quad (30)$$

TABLE III. Position (in cm^{-1} relative to the X asymptote) and nonradiative lifetimes (in microsecond) for the vibrational levels of the A state using the diabatic representation and the exact close coupling approach and comparison of the various results. v : vibrational level, E : vibronic energy, τ^a : non-radiative lifetime using the adiabatic approach, τ^{ac} : as before taking into account the adiabatic corrections, τ : close coupling nonradiative lifetime, τ^{Till} : nonradiative lifetime evaluated in Ref. 5.

v	E	τ^a	τ^{ac}	τ	τ^{Till}
0	6361.372	37.02	36.65	38.732	200.
1	6640.891	6.15	6.14	6.051	47.
2	6952.551	69.26	69.52	69.764	20.
3	7286.694	15.71	15.79	15.556	1.3
4	7638.031	9.27	9.41	8.722	
5	8002.252	10.11	9.94	10.669	
6	8376.111	2.45	2.44	2.455	
7	8757.115	4.32	4.34	4.299	
8	9142.933	35.81	36.88	33.924	
9	9531.552	6.79	6.71	7.255	
10	9921.292	1.04	1.04	1.073	
11	10310.550	0.50	0.50	0.506	
12	10697.905	0.51	0.52	0.516	
13	11082.018	1.07	1.07	1.031	
14	11461.599	6.36	6.39	5.299	
15	11835.356	84.98	84.50	263.711	
16	12201.983	6.56	6.56	7.992	
17	12560.081	18.20	18.19	19.504	
18	12908.047	11.83	11.87	14.874	
19	13243.938	0.98	0.99	1.143	
20	13565.344	0.35	0.35	0.335	
21	13869.169	0.22	0.22	0.241	
22	14151.157	0.19	0.19	0.212	
23	14405.188	0.20	0.20	0.214	
24	14622.373	0.27	0.27	0.294	
25	14789.432	0.46	0.47	0.491	
26	14887.429	1.29	1.32	1.380	

with Δ being the integration step. However, to compute and store the $\chi^{(\pm)}$ matrix over all the points of the grid and then perform these quadratures constitutes a formidable task. To avoid the total reconstruction of the wave function, since the magnitudes of interest are $a_j(E)$, a new numerical procedure is proposed in which the integral is being built up in parallel to the forward propagation to obtain $\mathcal{R}$. For that purpose, the vector M , with n_{op} components, is propagated according to the following scheme,

$$\begin{aligned}
 M_j(1) &= \sum_{i=1}^n B_i(1) \mathcal{R}_{i,j}(1), \\
 M_j(k) &= \sum_{i=1}^n [M_i(k-1) + B_i(k)] \mathcal{R}_{i,j}(k) \quad 2 \leq k \leq m-1, \\
 M_j(m) &= \Delta \sum_{i=1}^n [M_i(m-1) + B_i(m)] \chi_{i,j}(m) (I \mp iK)^{-1}.
 \end{aligned}
 \tag{31}$$

Finally, $a_j(E) \equiv M_j(m)$ as can be easily verified. Similar procedures have been successfully applied in previous works.¹⁶

FIG. 5. Comparison of amplitude density probabilities between adiabatic and diabatic schemes. Diamonds and squares: adiabatic approach for $v=0$ and $v=11$, respectively, in the A state. Full lines: corresponding diabatic results.

C. Results and discussion

Close coupling results are reported in Table III together with adiabatic Golden Rule ones (averaged over W_{XA} and W_{AX}) and also the previous estimations of Till *et al.*⁵ As illustrated in Fig. 4, the shift in the positions of the resonances is extremely small, comparable to the nonradiative widths and smaller than 10^{-5} cm^{-1} . Therefore, only vibronic positions are reported in Table III together with the nonradiative lifetimes but not these extremely small shifts. Except for $v=15$, the agreement with Golden Rule estimations is remarkable as can be expected for isolated and long life resonances. However, the present values are not in agreement with the estimations of Till *et al.*, perhaps due to the fact that part of the coupling was ignored in their approach and, in addition, their calculation relies on different $X\alpha$ potentials. In contrast with that estimation, where the lifetimes decrease monotonically as the vibrational level increases, our present results show an erratic evolution which should be related to the very unusual shape of the A state adiabatic potential. The vibrational levels 0, 2, 8, and 15 present a particularly long nonradiative lifetime, a characteristic which could be exploited in further experiments.

Finally, we compare the exact close coupling wave function and the adiabatic one. For that purpose the density probability is reported in Figure 5 for $v=0$ and $v=11$. At this scale it is not possible to distinguish the two approaches, an illustration of the adequation of the Born-Oppenheimer separation. To see differences we can compare the energies reported in Tables I, II, and III. Shifts of the order of magnitude of a few wave numbers can then be observed mainly due to the adiabatic corrections.

IV. CONCLUSION

Using diabatic and adiabatic representations, nonradiative lifetimes for all the vibrational levels of the A state have been accurately determined. The very good agreement between the various approaches despite they used completely

different couplings illustrates the accuracy of the present calculations and shows the validity of Golden Rule estimations. Small changes of the potentials have also been tested involving the adiabatic corrections. They do not lead to important modifications of the nonradiative lifetimes which appear as robust estimations with methodological as well as numerical stability. The nonradiative lifetimes for the *A* state are in the order of microseconds in agreement with previous estimations. However, they present large and rather erratic variations with the vibrational levels. We expect that the present contribution will encourage further experimental studies on this simplest heteroatomic molecule.

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