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A diabatic electronic state system to describe the internal conversion of azulene

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Abstract

A diabatic system of two electronic potential energy surfaces as well as the coupling between them is presented. The system is to be used to study the dynamics of the $S_1 \rightarrow S_0$ internal conversion of azulene and is based on single point calculations of the minima of the two surfaces and a dipole-quadrupole (DQ) diabaticization. Based on this, a couple of harmonic diabatic surfaces together with a linear coupling surface have been devised. Some preliminary dynamics results are shown.

Keywords

azulene; internal conversion; diabatic states

1 Introduction

The molecule of azulene is a well-known example of an exception to Kasha's rule, according to which fast spontaneous emission is only observed from the lowest excited state. In fact, azulene is known to decay from the first excited singlet state (S_1) to the ground state (S_0) through fast internal conversion induced by nonadiabatic coupling[1].

Internal conversion of azulene has been studied both theoretically and experimentally. A well established means of exploring dynamical processes is through the rate of decay of a state population[2–9]. Rentzepis[2] has determined a lifetime of 7 ps for the S_1 state in solution through a picosecond pump-and-probe experiment. The same lifetime was estimated to be 1.4 ps by Foggi et al. through femtosecond transient absorption. On the other hand, Amirav et al.[10] and Suzuki et al.[11], determined a lifetime of around 1.0 ps for the isolated molecule.

Theoretical calculations on the system include a full-CI optimization by Bearpark et al.[12] where a conical intersection at energies 1 – 13 kcal/mol above the minimum of the S_1 state was found. The presence of such a conical intersection was strengthened by an increase in the vibronic band broadening observed by Ruth et al.[13] using cavity ring-down absorption spectroscopy at a vibrational excess energy above $0 + 2177 \text{ cm}^{-1}$. The S_1 state was reported as having a lifetime of $900 \pm 100 \text{ fs}$ at a vibrational excess energy around 2000 cm^{-1} by

Zewail and coworkers[14] through femtosecond resolved mass spectrometry in a molecular beam.

In this paper we present a diabaticization of the lowest two electronic surfaces of azulene we have recently completed. This diabaticization was performed using the dipole-quadrupole (DQ) diabaticization method of Truhlar et al.[15]. The two surfaces are assumed to be harmonic while the diabatic coupling is linear. Subsequently, we intend to run quantum dynamics based on our Gaussian Multi-Configuration Time-Dependent Hartree (G-MCTDH)[16–18] algorithm to explore the internal conversion dynamics (the high dimensionality of the problem renders this scheme preferable with respect to others[19–24]). In particular, an exact time-dependent or time-independent calculation would be completely prohibitive, due to the high dimensionality of the problem. On the other hand, the diabatic coupling can be used, together with the calculation of the density of states of the molecule, to calculate an internal conversion rate using Fermi's Golden rule. However, such a calculation furnishes short-time information and does not give any insight on particular vibrational modes that can help or hinder internal conversion. The initial results of a preliminary dynamics calculation are also shown.

2 Calculation of the electronic PES

The diabatic coupling between the two lowest energy singlet states of azulene has been obtained by maximizing the difference between the dipole and quadrupole moments associated with the two states and the corresponding transition moments, by a rotation of the two states.

For a non-radiative transition between electronic states 1 and 2, the diabatic states can be expressed as a linear combination of two adiabatic states [15]:

$$\Psi_{dia} = \Psi_{adia,1}T_1 + \Psi_{adia,2}T_2 \quad (1)$$

where $\Psi_{adia,1}$ and $\Psi_{adia,2}$ are the adiabatic states. The T matrices perform the transformation of the adiabatic states to the diabatic ones Ψ_{dia} . In the DQ-diabatization approach, the diabatic states are represented as [15]

$$\begin{pmatrix} \Psi_{dia,1} \\ \Psi_{dia,2} \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \Psi_{adia,1} \\ \Psi_{adia,2} \end{pmatrix} \quad (2)$$

The mixing angle, θ is calculated by

$$\theta = \arctan(-B/A) \quad (3)$$

A and B are obtained from the transition dipole and quadrupole moments and the dipole and quadrupole moments of the adiabatic states:

$$B = \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_t - \boldsymbol{\mu}_t \cdot \boldsymbol{\mu}_2 + \alpha(M_1 M_t - M_t M_2) \quad (4)$$

and

$$A = -\frac{\mu_1^2 + \mu_2^2}{4} + \mu_t^2 + \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{2} - \frac{\alpha M_1^2}{4} + \frac{\alpha M_2^2}{4} - \alpha M_t^2 - \frac{\alpha M_1 M_2}{2} \quad (5)$$

The dipole moments of the two states are represented as $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$; μ_1 and μ_2 denote their magnitudes. M_1 and M_2 are traces of the quadrupole moments, while $\boldsymbol{\mu}_t$ and M_t are the transition dipole moment and trace of the transition quadrupole moment.

The relative contribution of the quadrupoles to the diabatic coupling is determined by the parameter α . The DQ-formalism reduces to the limit of Boys localisation in the extreme case of $\alpha=0$. Maximisation of the function F in terms of the adiabatic matrix elements [15] leads to the above relations,

$$F = \mu_1^2 + \mu_2^2 + \alpha(M_1^2 + M_2^2) + A + \sqrt{(A^2 + B^2)} \cos(4(\theta - \gamma)) \quad (6)$$

F being maximum when

$$\theta = \gamma, \gamma + \pi/2, \dots \quad (7)$$

At the Franck-Condon level of approximation, the coupling is calculated at the minimum geometry of the final state, *i.e.*, the electronic ground state.

The DFT and TD-DFT levels of theory have been used for obtaining the equilibrium geometries and corresponding force constants, for the ground (S_0) and excited states (S_1) of azulene, using the GAUSSIAN suite of programs[25]. The B3LYP [26] functional and the 6-31G(d) basis set [27] have been used. The dipole and quadrupole moments have been obtained at the TD-B3LYP/6-31G(d) level. All calculations have been done in the gas-phase.

Here, we mention that in a previous study [28] by some of the authors, we computed the temperature dependence of rates of non-radiative transitions where the non-adiabatic, momentum couplings between adiabatic electronic states were used to compute the rates. In that work, azulene was used as the test case to represent rigid molecules to validate the performance of our implementation. The (TD)-B3LYP/6-31G(d) level of theory was used there and showed to be a reliable electronic structure method for the prediction of the rate of $S_1 \rightarrow S_0$ internal conversion in azulene. Furthermore, the absorption spectrum for the $S_0 \rightarrow S_1$ (Fig. 1) was very well reproduced compared to the experiment [29] at the (TD)-B3LYP/6-31G(d) level of theory, therefore we used the same level of theory in our dynamics study.

Due to a negligible value of the trace of the transition quadrupole moment of azulene, a low value of the parameter α was considered, in order to reduce the weight of the quadrupole moments on the coupling. Following some test calculations, a 0.1% contribution of the quadrupoles was chosen, effectively reducing the case to the Boys-localization limit.

The diabatic coupling and its derivatives with respect to the normal coordinates have been calculated with a stand-alone code, by displacing each atom 0.001 angstrom to either side of the equilibrium geometry along each Cartesian coordinate.

3 Surface characteristics

Based on the frequencies of the normal modes around the minima of both ground and excited states, the diabatic surfaces have been modelled as a collection of uncoupled harmonic oscillators. Each surface contains a global minimum and the potential energy is given by a sum of parabolic potentials around it using the calculated frequencies. Besides the frequencies for each state, the system is characterized by the following parameters:

- The adiabatic transition energy between the electronic states, i.e. the difference in energy between the minima.
- The coordinates of the excited state minimum in terms of ground state normal coordinates.
- The Duschinsky matrix, relating the excited state normal coordinates to the ground state ones.

Thus, the energy of both ground and excited states is represented by the formula

$$E^{(s)}(q_1, \dots, q_{48}) = E_0^{(s)} + \frac{1}{2} \sum_{k=1}^{48} \omega_k^{(s)} (q_k^{(s)} - q_{k,0}^{(s)})^2 \quad (8)$$

where q_k denotes the k -th normal mode, its equilibrium position being $q_{k,0}$ (obviously, frequencies are different for ground and excited states). E_0 is assumed to be zero for the ground state, whereas it takes the value of the adiabatic energy difference of the two states for the excited one. The index (s) above the normal coordinates indicates that the energy of each state is expressed with respect to its proper normal coordinates. On the other hand, during a time-dependent propagation (which takes place in one set of normal coordinates), the non-unity of the Duschinsky matrix leads to corresponding linear terms in the potential energy.

Furthermore, in our model the diabatic coupling is assumed to be a linear function of all coordinates, based on its value and its gradient vector around the ground state minimum. Thus, the equation for the diabatic coupling is

$$V(q_1, \dots, q_{48}) = V_0 + \sum_{k=1}^{48} V_k (q_k - q_{k,0}) \quad (9)$$

In this equation, V_0 is the value of the diabatic coupling above the ground state minimum, whereas V_k are the derivatives of this coupling with respect to each normal coordinate. At each point, the 2×2 diabatic matrix can be diagonalized, yielding the adiabatic energies. These would be subject to nonadiabatic interaction due to the nuclear kinetic energy, which is difficult to handle computationally.

The frequencies of the 48 normal modes of both ground and excited states are given in Table 1.

4 Preliminary dynamics

In order to study the dynamics of the internal conversion of azulene, we have used the G-MCTDH code developed previously by us. This code gives us various possibilities to investigate the dynamics of azulene from a quantum mechanical point of view. In particular:

1. A full variational multi-configuration Gaussian (v-MCG) calculation can be performed. In this case, the nuclear wavefunction of the system is written as

$$\Psi(r, t) = \sum_{k=1}^n c_k g_k(r_1, r_2, \dots, r_{48}, t) \quad (10)$$

where each g_k is a product of Gaussians over the 48 vibrational degrees of freedom. This Gaussian evolves with time, being continually displaced in coordinate and momentum space. This way of expanding the wavefunction corresponds to a linear combination of n trajectories. For $n = 1$ we get an ordinary classical simulation, whereas as n tends to infinity we get convergence to full quantum mechanics.

2. Once a clearer picture of the dynamics is obtained, the vibrational degrees of freedom can be separated into "background" (or "bath") degrees of freedom, which do not have a significant role in the dynamics, and "principal" degrees of freedom. These latter ones need to be described more accurately than the background ones and, as a result, the wavefunction describing them is a linear combination of two or more Gaussians. In other words, the nuclear wavefunction is written (for m principal degrees of freedom) as

$$\Psi(r, t) = \sum_{k=1}^n c_k g_k(r_1, r_2, \dots, r_m, t) \times g_{bath}(r_{m+1}, \dots, r_{48}, t) \quad (11)$$

where the principal part of the wavefunction is evolved in parallel with a single quantum trajectory.

Moreover, the treatment of the two diabatic surfaces also needs to be considered. The simplest treatment is the complete *single-set* formalism, whereby the same nuclear

wavefunction is used for both surfaces. In this case, the complete (including the electronic degree of freedom) wavefunction is given by the formula

$$\Psi = \sum_{k=1}^n d_k |s_k\rangle \times \psi_{nuc}(r, t) \quad (12)$$

Thus the electronic degree of freedom is simply treated as an extra dimension in the G-MCTDH formalism and the calculation is akin to an Ehrenfest one.

Alternatively, the code permits us to propagate a different nuclear wavefunction on each surface, i.e. to use the *multi-set* formalism. Such a treatment is necessary, for example, in dealing with photodissociation problems where dissociation occurs only on one surface. On the other hand, if the issue is simply the time-evolving populations on the surfaces (and the forces on the surfaces are not very different) then an Ehrenfest calculation can at least give a qualitative picture of the dynamics.

We have run a preliminary propagation on the two-surface system. The calculation is a simple Ehrenfest one, where one single Gaussian wavepacket is propagated on both surfaces, its coordinates and surface amplitudes evolving with time in a variational manner. Therefore, the wavefunction propagated is of the form

$$\Psi(r, t) = g[r(t)] \times (c_g(t) |GS\rangle + c_e(t) |ES\rangle) \quad (13)$$

where $r(t)$ represents the trajectory followed by the wavepacket and c_g, c_e are the coefficients of the ground and excited states respectively. The initial conditions were $c_g(0) = 0, c_e(0) = 1$ (i.e. the wavepacket starts entirely in the excited state), while the coordinates of the wavepacket correspond to the excited state minimum (as it is essentially the zero-level lifetime that has been measured).

In Fig. 2 are shown the results of the propagation for the first 10000 atomic units of time (corresponding to around 0.2 ps). In the lower panel is shown the population of the ground state (initially zero) while in the upper panel is shown the ratio of the diabatic coupling to the energy separation of the two surfaces. If the coupling were zero, there would be no evolution at all as the wavepacket is found above the surface minimum. The diabatic coupling induces a degree of transfer to the lower surface, which causes a displacement of the wavepacket in coordinate space. As can be seen, as time progresses, the wavepacket is gradually exploring regions of higher intersurface coupling. The effect of this can be seen in the lower panel, where the Rabi oscillations between the surfaces gradually rise in amplitude.

5 Conclusions

Our diabaticization scheme, based on dipole and quadrupole moments, has yielded a surface that is expected to reproduce well the first-excited state dynamics of azulene, in particular its

internal conversion process from S_1 to S_0 . The small degree of intersurface coupling around the minimum of the excited S_1 state implies that

- The diabatic and adiabatic pictures are very close in this region, and therefore the approximation of the initial wavepacket as confined to the upper diabatic state is good.
- The internal conversion dynamics is expected to be well over the picosecond range (as also seen in measurements).

More detailed dynamics calculations, with a view to determine the critical points of the conical intersection seam as well as the particular normal modes governing passage between surfaces, are under way. In particular, possible ways to improve the results include:

1. Simulating the overall wavefunction in a more realistic way, dedicating more Gaussian functions in its description (at least for the principal degrees of freedom), as well as utilizing a multi-set formalism for the two surfaces.
2. Taking into account anharmonicity, simulating the potential energy function with appropriate Morse or Gaussian forms.

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Fig. 1.
A representation of the azulene molecule

Fig. 2.

The vibrationally resolved absorption spectrum for $S_0 \rightarrow S_1$ transition in azulene at the B3LYP/6-31G(d) level of theory. The spectrum compares very well with the experimental spectrum (Fig. 3 in Ref. [29]).

Fig. 3.
Small-time dynamics of azulene in a preliminary Ehrenfest calculation

Table 1Frequencies of azulene for both S_0 and S_1 states

Mode	GS frequency (cm^{-1})	ES frequency (cm^{-1})
1	117.981015	163.501597
2	192.662651	170.926311
3	277.256104	322.322986
4	336.034811	340.039919
5	391.897513	413.281252
6	407.212341	430.915084
7	503.395716	499.552709
8	505.41282	576.448949
9	574.103945	614.342818
10	670.849221	680.073437
11	678.597735	728.622826
12	694.762664	742.21335
13	731.621231	746.492958
14	762.735388	787.877933
15	770.800402	804.602064
16	823.313698	833.869817
17	864.009372	883.133207
18	878.618399	919.235272
19	894.605128	946.720822
20	920.960876	961.369049
21	937.590106	984.275191
22	987.607497	1004.03833
23	998.112016	1022.58126
24	1044.6671	1023.18486
25	1083.51897	1065.73774
26	1092.81379	1082.19057
27	1168.64483	1187.29696
28	1222.33232	1242.92626
29	1237.69275	1244.07286
30	1254.14728	1299.15926
31	1275.64852	1324.75001
32	1358.48597	1338.71704
33	1400.16985	1419.94548
34	1423.13679	1430.4382
35	1465.30507	1488.19761
36	1488.96751	1492.02871
37	1535.51969	1527.75368
38	1589.25069	1580.56148
39	1599.63041	1627.64896

Mode	GS frequency (cm ⁻¹)	ES frequency (cm ⁻¹)
40	1682.23746	1640.92519
41	3137.83171	3134.414
42	3141.31682	3136.12121
43	3168.60977	3144.60892
44	3170.11727	3163.53716
45	3181.19379	3172.10287
46	3210.30004	3201.85843
47	3214.09555	3219.14136
48	3244.2273	3227.72017