

Spin-orbit coupling in complexes of toluene with rare gas atoms

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The potential energy surfaces (PESs) and S_1 - T_1 spin-orbit coupling matrix element (SOCME) surfaces are investigated for the toluene-X weakly-bound clusters (X = Ne, Ar, and Kr). Calculations of the vibrational wave functions using a one-dimensional stretch model are presented and used to determine vibrationally-averaged values of the SOCMEs. Our *ab initio* theoretical results compare well with intersystem crossing rates derived from recent experimental fluorescence lifetime data [R. J. Doyle, E. S. J. Love, R. Da Campo, S. R. Mackenzie, J. Chem. Phys. **122**, 194315]. Vibrational averaging is shown to change the absolute magnitude of the calculated SOCMEs, but the ratio between them remains very similar to that of the single-point values calculated at the minima of the PESs.

I. INTRODUCTION

The nonradiative decay of electronically excited molecules and clusters is a topic of considerable current interest in the fields of molecular properties and reaction dynamics.¹⁻³ It is well known that the decay of excited states to other states of different multiplicity can occur via spin-orbit coupling, and the magnitude of this coupling can be highly sensitive to the local environment. Such effects have long been known in solution, where different solvents can lead to substantial changes in fluorescence lifetimes. In this context the phenomenon is known as the external heavy atom effect.⁴

Several studies have shown that in isolated and weakly-bound molecular clusters, the nearby presence of a single rare gas atom can greatly influence the decay dynamics of a molecule's excited state, by altering the magnitude of the spin-orbit coupling. Such a microscopic external heavy atom effect has been observed experimentally in rare gas van der Waals clusters of aromatic molecules including tetracene,^{5,6} pentacene,⁷ octatetraene,⁸ azulene,⁹ substituted anthracenes,^{10,11} para-difluorobenzene,¹² and toluene¹³.

Calculations of external heavy atom effects in clusters range from approximate treatments using the atomic spin-orbit coupling values⁹ to more advanced methods treating the entire cluster. Non-relativistic *ab initio* calculations of spin-orbit coupling in weakly-bound clusters have mainly been restricted to small systems containing five or fewer atoms. For example, Minaev *et al.* have used response calculations to study phosphorescence rates in C_2H_2 -X model systems (X=F⁻, Cl⁻, Br⁻, HCl, and Ar).¹⁴ An example of calculations treating larger systems is our previous experimental and theoretical study of para-difluorobenzene (pDFB) clustered with rare gas atoms,¹² in which we calculated vibrationally averaged singlet-triplet spin-orbit coupling matrix elements

(SOCMEs) using a linear response approach.

In this paper we show that modern *ab initio* techniques can account quantitatively for the trend in lifetimes of the S_1 state of the toluene-X (X=Ne, Ar, Kr) clusters with increasingly heavy cluster partner. We make use of multiconfigurational linear response theory, which enables the direct calculation of the singlet-triplet coupling matrix element without the explicit calculation of the triplet state wave function. We map out the magnitude of the coupling matrix element over a range of cluster geometries commensurate with the global minimum on the calculated intermolecular potential energy surface. Furthermore, we investigate the S_1 state potential energy surfaces of these systems and calculate vibrational wave functions for the relative motion of the cluster components in a restricted model. The vibrational averaging is shown to change slightly the absolute magnitude of the calculated SOCMEs, but the ratio between them remains almost identical to that of the single-point values calculated at the minima of the PESs. Both of the calculated ratios agree with the corresponding experimental ratio, within the reported uncertainties.

II. POTENTIAL ENERGY CALCULATIONS

We have performed electronic structure calculations on the toluene-rare gas systems, with the aim of determining a suitable model of the interaction potential for use in the calculation of vibrational levels. In our earlier work on the higher symmetry pDFB-rare gas systems,¹² we employed a simple representation where the motion of the rare gas atom was restricted to a line perpendicular to the aromatic ring and passing through its centre. Such a model may be considered less appropriate for the toluene-rare gas clusters, because toluene is lower in symmetry than pDFB, and the minimum-energy path

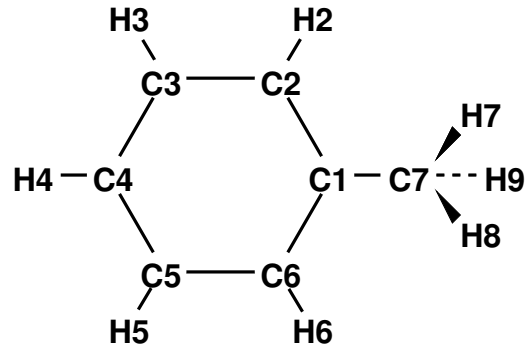
along the potential surface deviates from the normal to the ring (hereafter termed the R -axis). However, as will be made clear below, the toluene-rare gas potentials are determined in this work to be roughly symmetric around the R -axis, indicating that the one-dimensional stretch model is in fact suitable as a first approximation.

The equilibrium geometry of the isolated toluene molecule in the excited S_1 state was first optimised, and then held fixed throughout the potential energy calculations. The justification for this is that the experiments with which we wish to make comparison were performed on the vibrationless S_1 levels.¹³ Also, the relatively low-frequency van der Waals modes of interest are not expected to greatly perturb the toluene geometry. The complete-active-space self-consistent field (CASSCF) method¹⁵ with six electrons in the π space of six active orbitals, and the aug-cc-pVDZ basis set,^{16–18} was used for the optimisation. The resulting geometry is detailed in Table I. The vibrational frequencies for the optimised structure are real, and the methyl group hydrogens are staggered with respect to the ring. For comparison the table also lists the geometry described by East *et al.*¹⁹, who combined experimental fluorescence data with calculated CASSCF/6-31G(d,p) results in a least-squares fit (referred to as LSQ II).

The cluster potential energy data was generated using the MOLCAS package²⁰ with the CASPT2 method and the aug-cc-pVDZ basis set. Core orbitals on both toluene and the noble gas atoms were frozen and only valence electrons correlated for all CASPT2 calculations. The inclusion of core-valence correlation would be expected to increase the depth of the interaction potential somewhat for the Ar and Kr clusters, since it will increase the calculated polarizability. At the present level of accuracy this can be ignored. Counterpoise calculations were carried out at each point to mitigate against basis set superposition error (BSSE) using the method of Boys and Bernardi²¹. Intruder state problems were encountered with the CASPT2 calculations and resolved by using an imaginary level shift as devised by Forsberg and Malmqvist²².

The R, x, y coordinate system used in this work for specifying the location of the rare gas nucleus relative to the toluene molecules is depicted in Fig. 1. At its equilibrium geometry, toluene assumes the C_s point group and the potential is symmetric on each side of the symmetry plane. The origin of the coordinate system was chosen as the mid-point between the C1 and C4 atoms on the C_s axis. The variation in the potential along x is mapped-out in Fig. 2 at fixed $R=3.374$ Å. It can be seen that the potential is almost symmetric about $x=0$. As expected, the potential is similar to those calculated for other aromatic ring-rare gas systems, where global potential minima are found above the center of the rings.^{23–27} Our potential curves along the R axis are shown in Fig. 3. These curves were used in the approximate treatment of the vibrational averaging in section IV.

TABLE I: Optimised geometry of the S_1 state toluene molecule using CASSCF/aug-cc-pVDZ, compared with “LSQ II” data from Ref. 19 where their torsional angle $\rho=90^\circ$ (i.e., the staggered conformation). R_{AB} refers to the distance in Å between nuclei of A and B, and \angle_{ABC} refers to the angle in degrees between the B→A and B→C vectors.



Property	CASSCF	LSQ II
$R_{C1,C7}$	1.504	1.499
$R_{C1,C2}$	1.441	1.439
$R_{C2,C3}$	1.436	—
$R_{C3,C4}$	1.434	1.432
$R_{C2,H2}$	1.079	1.084
$R_{C3,H3}$	1.079	1.084
$R_{C4,H4}$	1.079	1.084
$R_{C7,H9}$	1.094	1.101
$R_{C7,H7}$	1.090	—
$\angle_{C2,C1,C6}$	119	119
$\angle_{C1,C2,C3}$	121	—
$\angle_{C2,C3,C4}$	120	—
$\angle_{C3,C4,C5}$	120	120

III. SPIN-ORBIT COUPLING MATRIX ELEMENTS

In order to determine the interaction between the singlet $|S_1\rangle$ and triplet $|T_1\rangle$ electronic states for the toluene-X systems, calculations of the appropriate matrix elements of the spin-orbit operator were performed. We have calculated these matrix elements as residues of a triplet linear response function²⁸, with a multiconfigurational reference $|S_1\rangle$ wave function,

$$\langle S_1 | H_{so} | T_1 \rangle = \lim_{E \rightarrow E_{T_1 S_1}} (E - E_{T_1 S_1}) \langle \langle H_{so}; V(E) \rangle \rangle_E, \quad (1)$$

where V is an excitation operator and $E_{T_1 S_1}$ is the energy gap between the singlet and triplet states. H_{so} is the spin-orbit operator, for which we employed the mean-field formulation of Heß *et al.*²⁹. The S_1 CASSCF state was calculated with a (6/6) pi electron active space and the aug-cc-pVDZ basis set. These multiconfigurational linear response (MCLR) calculations were performed using the DALTON quantum chemistry program³⁰. We

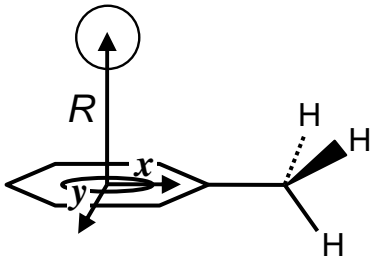


FIG. 1: Schematic diagram defining the coordinate system used in this work.

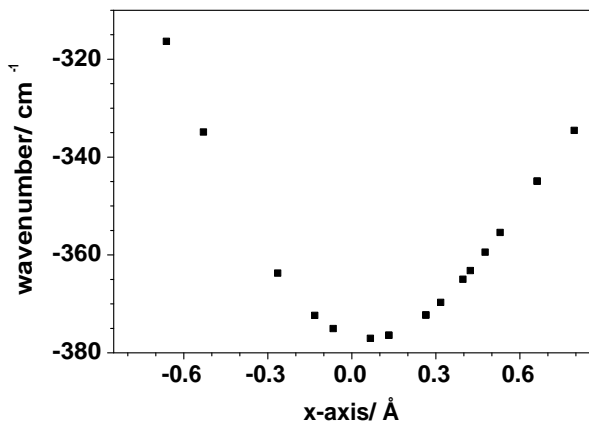


FIG. 2: A cut through the toluene-Ar S_1 potential surface, for $y=0$ and $R=3.374$ Å.

should perhaps note that since the MCLR calculations are performed in a determinantal basis, without explicit spin adaptation, it is occasionally the case that the S_0 state appears as the lowest energy “excited state”, but the desired T_1 state is easily obtained by taking an extra root of the MCLR equations.

Matrix elements were calculated for a range of rare-gas coordinates in the x - R plane. Coordinates for the position of the rare gas atom with $+R$ are not equivalent to those with $-R$ (i.e., for the rare gas atom reflected in the plane of the ring), due to the presence of the methyl group. However, it may be expected that the differences in the matrix elements for $\pm R$ are negligibly small in the region around the center of the ring. In order to test this assumption, calculations were performed for toluene-Ar covering both sides of the ring. As can be seen in Fig. 4 the variation between the values on each side, around $x=0$, is small and all further calculations were performed on one side only (the side with $R > 0$ in Fig. 1). The origin of the asymmetry in the SOCMEs further away from $x=0$ may involve the slight non-planarity of the ring due to the methyl group.

Contour plots for the matrix elements of toluene-Ne

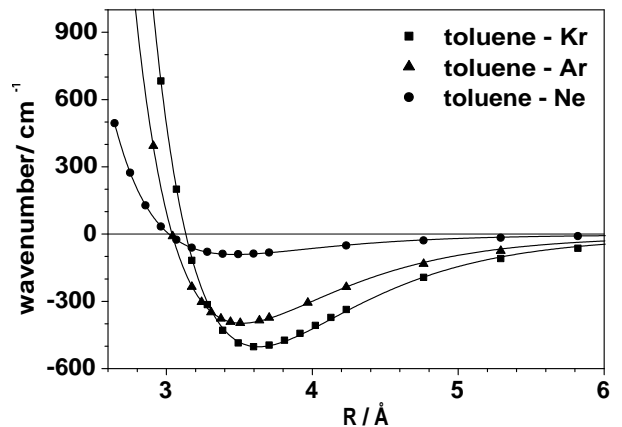


FIG. 3: S_1 state potential energy curves for toluene-X ($X=Ne, Ar, Kr$) shown as a function of R for $x=y=0$.

and toluene-Kr are shown in Figs. 5 and 6 respectively. For comparison, the matrix elements for all three clusters are plotted along the R -axis in Fig. 7. In the limit of large R , the SOCMEs converge to the same asymptotic value of 0.1215 cm^{-1} . This wavenumber corresponds in principle to the SOCME for toluene, unperturbed by the presence of a cluster partner. However, this value is not expected to be numerically accurate because of the difficulty in calculating SOCMEs of such small magnitude using the current level of theory.

IV. VIBRATIONAL AVERAGING AND COMPARISON WITH EXPERIMENT

Experimentally, the fluorescence lifetimes of the toluene-rare gas atom S_1 states have been shown to vary considerably from 44 ns for toluene-Ar to 4 ns for toluene-Kr, in comparison to 84 ns for the uncomplexed toluene molecule.¹³ Such lifetimes are longer than the equivalents for para-difluorobenzene.¹² It has previously been argued that the explanation for this trend lies in the increase in SOC between S_1 and T_1 with the presence of more massive rare gas atoms in the clusters.¹³ If this is the case, the ratio of the experimental fluorescence decay rates should agree with the ratio of the calculated SOCMEs. One simple (semiclassical) way to make such a comparison is to take the values of the SOC matrix elements for the equilibrium geometries, i.e., for the R coordinate where the potential curves are at their minimum. One step up from this semiclassical approach is to allow the rare gas atom to move along the R axis relative to toluene, and determine the energy and wavefunction for the lowest-energy ($v=0$) quantum level of this one-dimensional model. The SOCME can then be averaged over this vibrational motion. In other words, the expectation value of the SOCME is determined for the lowest-energy vibration of S_1 . The Hamiltonian for the model

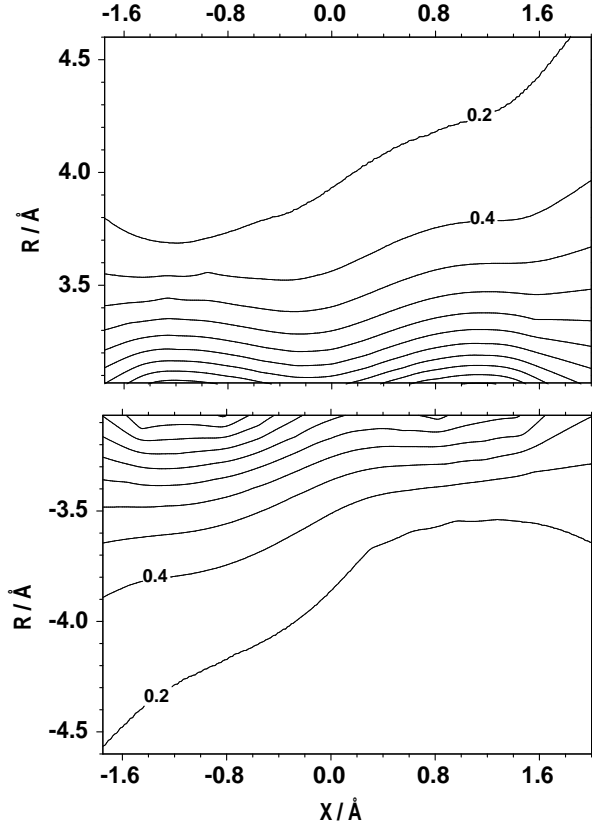


FIG. 4: Contour plot of the SOCME surface for toluene-Ar. The contours are equally spaced in steps of 0.2 cm^{-1} .

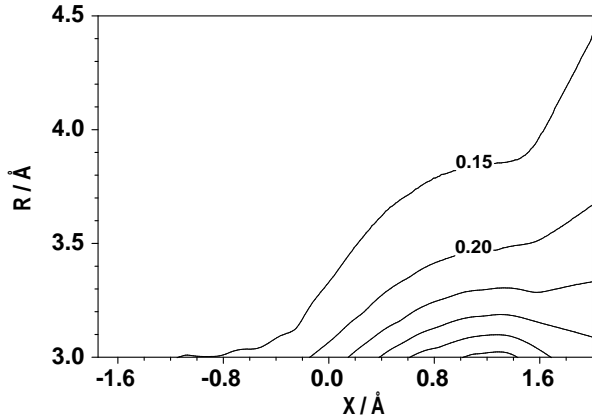


FIG. 5: Contour plot of the SOCME surface for toluene-Ne. The contours are equally spaced in steps of 0.05 cm^{-1} .

one-dimensional stretch systems can be written as

$$\hat{H} = \frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR'^2} \right) + \hat{V}(R'), \quad (2)$$

where μ is the reduced mass of the toluene-X system, R' is the distance between the rare gas atom and the center-of-mass of toluene, and \hat{V} is the potential energy operator. The vibrational energies and wave

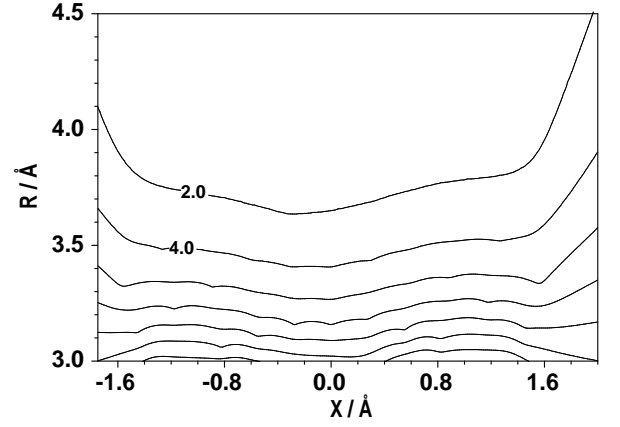


FIG. 6: Contour plot of the SOCME surface for toluene-Kr. The contours are equally spaced in steps of 2 cm^{-1} .

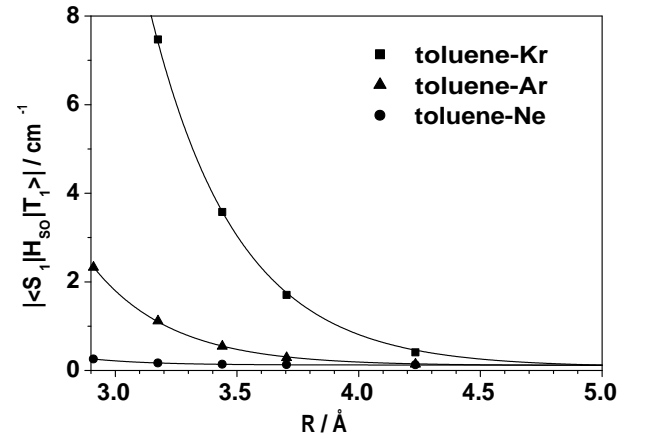


FIG. 7: Cuts through the SOCME surfaces at $x = y = 0$. The symbols indicate the calculated data points, whilst the solid lines are least-squares fits to exponential decays.

functions were generated by diagonalising \hat{H} in a basis of sinc-DVR (Discrete Variable Representation)³¹ functions. The overlap integral of the square of the ground-state ($v=0$) wave function with the calculated SOCME data provides the vibrationally-averaged value of the SOCME. A comparison of the vibrationally-averaged, semiclassical and experimental data is presented in Table II. The experimental data is presented in terms of Γ_{HA} (Heavy Atom) values, defined as the difference in the nonradiative decay rate between the clustered and unclustered molecule^{12,13}. This parameter reflects the experimentally-determined *increase* in the rate of spin-orbit coupling upon clustering^{12,13}. According to Fermi's golden rule, the $T_1 \leftarrow S_1$ transition rate is proportional to the square of the SOCME. In order to make a comparison between our theoretical calculations and the experimental Γ_{HA} values, it is necessary to determine the squares of the calculated SOCMEs and subtract the contribution from the bare toluene molecule. This gives us a theoretical prediction for the relative *increases* in the transi-

tion rate due to clustering. The ratio of these adjusted squared SOCMEs can then be compared with the ratio of the experimental Γ_{HA} values. In Table II, the squared SOCMEs have been adjusted as described above by subtracting their asymptotic values, and the appropriate ratios are compared. The theoretical ratios for both the single-point and vibrationally-averaged values fall well within the uncertainties in the experimental ratio. The vibrational averaging procedure alters the magnitude of the SOCMEs to some extent: for the toluene-Ne complex the value is slightly reduced, whereas for the other two species the SOCME is increased. However, the ratio of the squares of the vibrationally-averaged SOCMEs is very similar to that for the single-point values and both fall well within the range of experimental uncertainty.

In conclusion, the calculated SOCMEs for clusters of toluene with rare-gas atoms agree well when compared to the experimental data at its current level of accuracy. A simple vibrational-averaging procedure slightly alters the absolute magnitude of the SOCMEs, but the ratio between them remains very similar to the ratio of the SOCMEs calculated at the minima of the potential surfaces.

V. SUMMARY

We have presented calculations of potential energy surfaces and SOCMEs for a range of toluene-rare gas atom clusters, and have determined vibrationally-averaged values for the SOCMEs. These compare very well with experimentally-derived fluorescence lifetime data, supporting the explanation that spin-orbit coupling from the S_1 to the T_1 state is responsible for the trends in lifetimes observed.

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TABLE II: Calculated SOCMEs and experimental decay rates for S_1 cluster states. The experimental ratio is given as the ratio of Γ_{HA} values from Ref. 13

Species	$ \langle S_1 H_{\text{so}} T_1 \rangle ^2$		Ratio		
	value at R_e	vibrationally-averaged	value at R_e	vibrationally-averaged	Experimental ratio
toluene-Ne	3.94×10^{-3}	3.87×10^{-3}	2.04×10^{-2}	1.93×10^{-2}	0.08 ± 0.1
toluene-Ar	0.193	0.200	1.00	1.00	1.00
toluene-Kr	4.55	4.70	23.5	23.5	22.6 ± 12