# Effect of a magnetic field on an $E\otimes\epsilon$ Jahn-Teller system: Berry phase and optical properties

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We have studied the effect of a uniform magnetic field on Berry phase (BP) and optical properties (absorption for right-hand and left-hand circularly polarized light) of an $E\otimes\epsilon$ Jahn-Teller (JT) system. The magnetic field is applied along the trigonal axis of a trigonal-symmetry compound. Dynamical properties are exactly determined in the framework of the Lanczos algorithm, because the coefficients of the recursion procedure can be put in analytic form. Different strength of linear electron-phonon coupling and magnetic field are studied, and the connection with BP is analyzed.

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The Jahn-Teller (JT) effect[1] due to the nonadiabatic coupling of degenerate normal vibrations to the electronic motion influences different systems (molecules, ions, impurities, cluster, etc.).[2–5] The $E\otimes\epsilon$ JT system describes any orbital (non-Kramer) doublet, belonging to a double degenerate irreducible representation, interacting with a two-dimensional mode of $\epsilon$ symmetry. It has been extensively studied[6–8] for its prototype character, which well fits a large variety of molecular systems and it continues to present interesting and remarkable aspects linked to conical intersections and to the Berry phase (BP).[9] However, only marginal attention has been devoted to the effect of an external magnetic field.[10,11]

Here we propose the study of the effect of a uniform magnetic field applied along the trigonal axis of a trigonal-symmetry compound. We start with the calculation of BP (Refs. 12–14) by means of a general procedure; then optical properties of this system, in particular the absorptions for right-hand and left-hand circularly polarized light, are studied for different values of the applied magnetic field.

The vibronic Hamiltonian $H$ for a linear $E\otimes\epsilon$ JT system has the well-known form

$$H=T_N+U=\frac{1}{2}\hbar\omega[(p_\theta{}^2+p_\epsilon{}^2)+(q_\theta{}^2+q_\epsilon{}^2)]\sigma_0+\hbar\omega\boldsymbol{G}\cdot\boldsymbol{\sigma}, \tag{1}$$

where $T_N$ and $U$ are, respectively, the kinetic and potential energy. The vector $\boldsymbol{G}$ is defined as

$$\begin{aligned} G_x&=\|\boldsymbol{G}\|\sin\beta\cos\alpha=-kq_\theta \\ G_y&=\|\boldsymbol{G}\|\sin\beta\sin\alpha=kq_\epsilon \\ G_z&=\|\boldsymbol{G}\|\cos\beta=\Delta; \end{aligned} \tag{2}$$

the components $\sigma_x$, $\sigma_y$, and $\sigma_z$ of $\boldsymbol{\sigma}$ are the usual Pauli matrices; $k$ is the dimensionless linear coupling constant; and $G_z=\Delta=\mu B/\hbar\omega$ represents the applied magnetic field in units of $\hbar\omega$. Notice that a similar $G_z$ contribution could also be produced by the spin-orbit coupling.[15]

The eigenvalues of $U$ give us the Adiabatic Potential Energy Surfaces (APES) $W_\pm$ (in units of $\hbar\omega$):

$$W_\pm(q)=\frac{1}{2}(q_\theta{}^2+q_\epsilon{}^2)\pm\|\boldsymbol{G}\|=\frac{1}{2}\rho^2\pm\sqrt{\Delta^2+k^2\rho^2},$$

where we have introduced the dimensionless polar coordinates $(\rho,\theta)$ in the usual form $q_\theta=\rho\cos\theta$, $q_\epsilon=\rho\sin\theta$ in the $(q_\theta,q_\epsilon)$ plane. Due to the effect of the applied magnetic field, at $\varrho=0$ the double degenerate vibronic levels are split and the conical intersection is removed. In Fig. 1 the APES are plotted for $\Delta>k^2$ (left) and for $\Delta<k^2$ (right).

The explicit form of the eigenfunctions $\psi_\pm$ can be obtained from the transformation that diagonalizes the potential energy term $\boldsymbol{G}\cdot\boldsymbol{\sigma}$.[16] It is a simple matter to show that the eigenfunctions are:

$$\psi_+=\begin{pmatrix}\cos\dfrac{\beta}{2}\\ \sin\dfrac{\beta}{2}e^{i\alpha}\end{pmatrix}\quad \psi_-=\begin{pmatrix}-\sin\dfrac{\beta}{2}e^{-i\alpha}\\ \cos\dfrac{\beta}{2}\end{pmatrix}. \tag{3}$$

Insofar as the quantum electron-phonon coupling is exactly diagonalized, the BP concept is implicitly embodied in the exact results. However, it remains a valuable concept for a deeper understanding of the JT systems.[17,9] For our system the ground adiabatic energy surface, as well as the excited one, are always nondegenerate. We can consider any circuit $C$ and denote by $S$ the surface of contour $C$. The BP

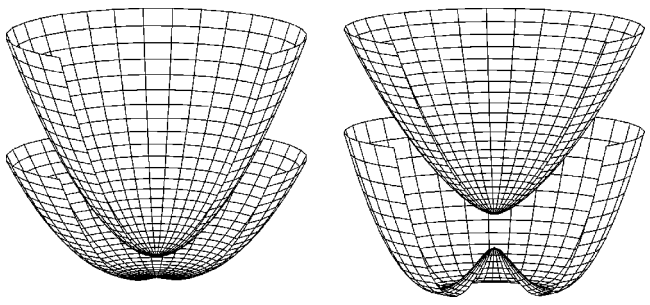

FIG. 1. APES for the $E\otimes\epsilon$ Jahn-Teller system with a magnetic field $\Delta$. On the left is sketched the case $\Delta>k^2$ whereas the case $\Delta<k^2$ is on the right.

 

$$\gamma_{\pm}(C)=\oint_C \mathcal{A}_{\pm}\cdot \mathrm{d}\boldsymbol{l}=\int_S \mathcal{B}_{\pm}\cdot \mathrm{d}S \tag{4}$$

can be explicitly calculated taking into account that the ''fictitious vector potential'' is

$$\mathcal{A}_{\pm}\equiv i\langle\psi_{\pm}|\nabla\psi_{\pm}\rangle, \tag{5}$$

and the associated ''fictitious magnetic field'' is

$$\mathcal{B}_{\pm}\equiv\nabla\times\mathcal{A}_{\pm}. \tag{6}$$

By means of the explicit form of the eigenfunctions, the fictitious vector potential and the fictitious magnetic field are given by:

$$\mathcal{A}_{\pm}=\mp\sin^2\left(\frac{\beta}{2}\right)\nabla\alpha \tag{7}$$

$$\mathcal{B}_{\pm}=\pm\frac{1}{2}\sin\beta\nabla\alpha\times\nabla\beta. \tag{8}$$

Using Eqs. (2) an expression for $\nabla\alpha$ and $\nabla\beta$ can be obtained and with some manipulations we have

$$\mathcal{B}_{\pm}=\pm\frac{1}{2}\Delta\frac{k^2}{[\Delta^2+k^2\rho^2]^{3/2}}\boldsymbol{e}_z=\mp\frac{1}{2}\frac{\partial}{\partial\Delta}\frac{k^2}{\sqrt{\Delta^2+k^2\rho^2}}\boldsymbol{e}_z, \tag{9}$$

where $\boldsymbol{e}_z$ is the unit vector orthogonal to the $(q_\theta,q_\epsilon)$ plane. Then the expression of the BP for a circuit constituted by a circumference of radius $R$ around the origin can be put in the form

$$\gamma_{\pm}(C)=\mp\frac{1}{2}\frac{\partial}{\partial\Delta}\int_0^R\rho\,\mathrm{d}\rho\int_0^{2\pi}\frac{k^2}{\sqrt{\Delta^2+k^2\rho^2}}\mathrm{d}\theta$$

$$=\pm\pi\left(1-\frac{\Delta}{\sqrt{\Delta^2+k^2R^2}}\right), \tag{10}$$

Notice that, ''mutatis mutandis,'' this result is a special case of that of Berry.[12] Moreover in the limit $\Delta\to 0$ one recovers the well-known result for the linear $E\otimes\epsilon$ JT system: the BP of $\pi$ is related to the minus sign[7] acquired by real electronic wave functions after completing one loop. It must be compensated by another minus sign of the vibrational counterpart since the overall vibronic wavefunctions must be a well behaved single valued wave functions. This is a textbook example of antiperiodic BP induced boundary conditions that select the half odd integer for the angular momentum eigenvalues [see Eq. (12)] rejecting the ordinary integer ones. It can be shown[17] that in this case the ground state must be degenerate. Instead in the case of $\Delta\to\infty$ the BP vanishes and no ''unorthodox'' boundary conditions are to be considered; then the ground state of the system is expected to be nondegenerate.

To check this point we have to study dynamical properties. It is convenient to rewrite the corresponding Hamiltonian in the second quantization scheme and then apply the Lanczos recursion procedure.[18–20] Let us introduce the phonon creation and annihilation operator $a_\theta$, $a_\theta^\dagger$, $a_\epsilon$, $a_\epsilon^\dagger$ ($\theta$ and $\epsilon$ related to the two partners $q_\theta$ and to $q_\epsilon$ of the $\epsilon$ mode in the standard way). The Hamiltonian $H$ takes the form

$$H=\hbar\omega(a_\theta^\dagger a_\theta+a_\epsilon^\dagger a_\epsilon+1)\sigma_0+\hbar\omega\Delta\sigma_z$$
$$+\hbar\omega\sqrt{S}[-\sigma_x(a_\theta^\dagger+a_\theta)+\sigma_y(a_\epsilon^\dagger+a_\epsilon)], \tag{11}$$

where $S=k^2/2=E_{jt}/\hbar\omega$ is the Huang-Rhys factor. The basis functions are taken in the form $|\pm\rangle|n_\theta n_\epsilon\rangle$, where $|\pm\rangle$ are the electronic eigenfunctions of $\sigma_z$, and $|n_\theta n_\epsilon\rangle$ denote the two-dimensional harmonic oscillator eigenfunctions of phonon occupations numbers $n_\theta$ and $n_\epsilon$. Notice that the APES $W_\pm$ are invariant for any transformation $\theta\to\theta'$, so we have a continuous symmetry and the operator

$$J_z=L_z-\frac{1}{2}\sigma_z \quad \text{with} \quad L_z=-i(a_\theta^\dagger a_\epsilon-a_\epsilon^\dagger a_\theta) \tag{12}$$

is a constant of motion. Then the eigenstates of (11) can be classified with the eigenvalues $j$ of $J_z$, as in the classic linear $E\otimes\epsilon$ Jahn-Teller system.[6,7,22] Thus a representation which makes $J_z$ diagonal is a good starting point. Introducing the linear combinations

$$a_{\pm}=\frac{1}{\sqrt{2}}(a_\theta\mp ia_\epsilon) \tag{13}$$

it is easy to prove that $L_z$ assumes the diagonal form

$$L_z\to a_+^\dagger a_+-a_-^\dagger a_- \tag{14}$$

and the total Hamiltonian is transformed as

$$\tilde{H}=\hbar\omega(a_+^\dagger a_++a_-^\dagger a_-+1)\sigma_0+\hbar\omega\Delta\sigma_z$$
$$+-\hbar\omega\sqrt{2S}[\sigma_+(a_-+a_+^\dagger)+\sigma_-(a_++a_-^\dagger)], \tag{15}$$

where $\sigma_\pm=(\sigma_x\pm i\sigma_y)/2$. In the basis $\{|\pm\rangle|n_+n_-\rangle\}$ we have $j=n_+-n_-\mp 1/2$, and it is very easy to list the eigenstates of $H_0=\hbar\omega(a_+^\dagger a_++a_-^\dagger a_-+1)\sigma_0+\hbar\omega\Delta\sigma_z$ with the same $j$:

$$j=-\frac{1}{2}\to|+\rangle|00\rangle,\ |-\rangle|01\rangle,\ |+\rangle|11\rangle,\ |-\rangle|12\rangle,\ldots$$

$$j=+\frac{1}{2}\to|-\rangle|00\rangle,\ |+\rangle|10\rangle,\ |-\rangle|11\rangle,\ |+\rangle|21\rangle,\ldots$$

$$j=-\frac{3}{2}\to|+\rangle|01\rangle,\ |-\rangle|02\rangle,\ |+\rangle|12\rangle,\ |-\rangle|13\rangle,\ldots$$

$$\vdots$$

This table has some peculiar properties: the states in each row are listed in order of increasing $N=n_++n_-$; for a fixed $N$ there is only one state with a given $j$; and the first state of any row (i.e., the state with lower $N$) is of the form $|+\rangle|0,-j-1/2\rangle$ if $j<0$ and $|-\rangle|j-1/2,0\rangle$ if $j>0$. The linear Jahn-Teller interaction has nonzero matrix element only between the states with $N$ and those with $N\pm 1$. Thus if we use the first state of each row as initial state for the Lanczos

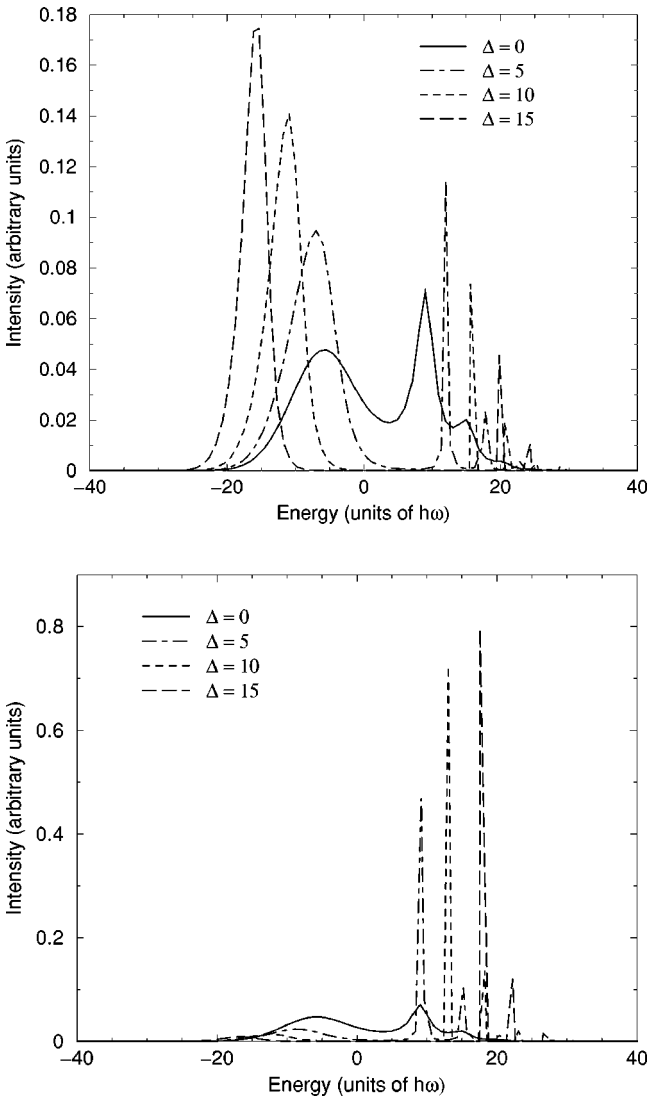


FIG. 2. Bandshape for the linear $E\otimes\epsilon$ Jahn-Teller system with magnetic field for the states with $j=-1/2$ (top) and $j=1/2$ (bottom). The Huang-Rhys factor is $S=40$ and the values of the magnetic field are shown in the figure.

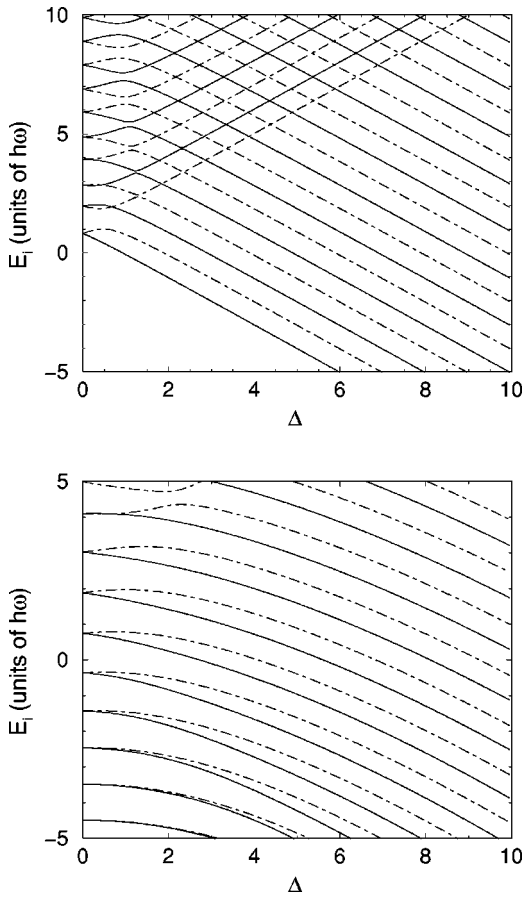


FIG. 3. Energy levels diagram for the $E\otimes\epsilon$ Jahn-Teller system with magnetic field for the states with $|j|=1/2$. The dot-dashed lines refer to the $j=1/2$ states while the solid ones to the $j=-1/2$ states. The Huang-Rhys factor is (from top to bottom) $S=0.1$ and $S=5$.

procedure we find that the $n$th state of the recursion coincides with the $n$th state of the row within an inessential phase factor. Moreover the coefficients $a_n$ and $b_n$ have an analytical form:

$$a_n(j)=\left(|j|+\frac{1}{2}+n+f(n,j)\Delta\right)\hbar\omega \quad n=0,1,2,\ldots \tag{16}$$

$$b_n^2(j)=[n+2|j|(n \mod 2)](\hbar\omega)^2 S \quad n=1,2,\ldots, \tag{17}$$

where the factor $f(n,j)$ is

$$f(n,j)=(-1)^{n+1-\mathrm{sign}(j)/2}=\begin{cases}(-1)^n & \text{if } j>0\\ (-1)^{n+1} & \text{if } j<0\end{cases}$$

and

$$n \mod 2=\begin{cases}0 & \text{if } n \text{ is even}\\ 1 & \text{if } n \text{ is odd}\end{cases}$$

If we put $\Delta=0$ we recover a well-known result: the states with angular momentum $\pm j$ are degenerate.[7]

The analytical expressions (16) and (17) for the coefficients of the recursion obviously avoid all the numerical problems of the Lanczos method.[21] The construction of the tridiagonal matrix or of the continued fraction expansion for the Green function is straightforward and the eigenvalues can be obtained within any desired accuracy.

In Fig. 2 we show the absorption spectrum of the $E\otimes\epsilon$ system and the modification of the band-shape due to the magnetic field.

In the case of a transition from a total symmetric state, we are mainly interested to the $j=1/2$ and $j=-1/2$ states of the $E\otimes\epsilon$ Jahn-Teller system. Notice that, increasing $\Delta$, the first main band is enhanced for the states with $j=-1/2$, while for $j=1/2$ the peaks of the Slonczewski resonances[23] become very sharp. Moreover there is a systematic shift towards lower and higher energies with respect to the case with

$\Delta=0$, that entails the Faraday effect. The same behavior is obtained for the states with higher values of $j$.

It is also of interest the energy levels diagram in presence of magnetic field. In Fig. 3 the energy levels diagram is shown for the states with $j=\pm 1/2$ for the values 0.1 and 5 of the Huang-Rhys factor $S$. We have observed a similar behavior for the states with higher value of the total angular momentum $j$.

It can be interesting to make a connection between the BP formalism and the calculated energy level diagram. For small $\Delta$ values ($\Delta<2S\equiv k^2$) we have seen that a maximum occurs in $\rho=0$ and that a circle of minima is located in $\rho=\rho_1=\sqrt{(4S^2-\Delta^2)/2S}$, so we can assume that the system, in its ground state, freely travels into this trough. Putting $R=\rho_1$ the expression (10) for the BP now becomes $-\pi(1-\Delta/2S)$. Then in the limit of $\Delta\ll 2S$ we reobtain the usual BP of $\pi$ and as a consequence the ground state of the system even in presence of a magnetic field remains ''quasi-degenerate'' [see for instance Fig. 3 (bottom), which refers to $S=5$, when $\Delta\ll 10$].

If $\Delta>2S$ we can think that the system, in its ground state, spends a considerable amount of time near the origin on the APES $W_-$. So in the expression (10) we can put $R=0$ obtaining no BP. In this case a non degenerate ground state is expected [see for instance Fig. 3 (top), which refers to $S=0.1$].

Out of these limits the BP is more complicated and depends on the radius of the trajectory (Eq. 11). However ultrafast optical absorption experiments, as proposed in Refs. 24 and 25, should in principle be sensitive to the BP changes produced by an external magnetic field. Moreover when adiabatic phase effects in angle resolved scattering experiments are detectable, they should also be influenced by an external magnetic field, so contributing to the debate about observable consequences of the BP in chemical reactions.[26–29]


[1] H.A. Jahn, and E. Teller, Proc. R. Soc. London, Ser. A **161**, 220 (1937).

[2] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972).

[3] I.B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer, Berlin 1989); I.B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds* (Wiley, New York, 1996).

[4] M.D. Kaplan and B.G. Vekhter, *Cooperative Phenomena in Jahn-Teller Crystals* (Plenum Press, New York, 1995).

[5] *Proceedings of the XIV International Symposium on Electron-Phonon Dynamics and Jahn-Teller Effect*, edited by G. Bevilacqua, L. Martinelli, and N. Terzi, (World Scientific, Singapore, 1999).

[6] W. Moffit and W. Thorson, Phys. Rev. **108**, 1251 (1957).

[7] H.C. Longuet-Higgins, U. Öpyk, M.H.L. Pryce, and H. Sack, Proc. R. Soc. London, Ser. A **244**, l (1958).

[8] M.C.M. O'Brien, Proc. R. Soc. London, Ser. A **281**, 323 (1964).

[9] H. Koizumi and I.B. Bersuker, Phys. Rev. Lett. **83**, 3009 (1999).

[10] L. Martinelli, M. Passaro, and G. Pastori Parravicini, Phys. Rev. B **43**, 8395 (1991).

[11] H. Koizumi and S. Sugano, J. Chem. Phys. **101**, 4903 (1994).

[12] M.V. Berry, Proc. R. Soc. London, Ser. A **392**, 45 (1984).

[13] A. Shapere and F. Wilczek, *Geometric Phases in Physics* (World Scientific, Singapore, 1989).

[14] M. Nakamura, *Geometry, Topology and Physics* (Adam Hilger, New York, 1990).

[15] A.J. Stone, Proc. R. Soc. London, Ser. A **351**, 141 (1976).

[16] G. Bevilacqua, Ph. D. thesis, University of Pisa (1999).

[17] F.S. Ham, Phys. Rev. Lett. **58**, 725 (1987); see also F.S. Ham, J. Phys.: Condens. Matter **2**, 1163 (1990).

[18] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950); **49**, 33 (1952); *Applied Analysis* (Prentice-Hall, Englewood Cliffs, 1956).

[19] R. Haydock, V. Heine, and M.J. Kelly, J. Phys. C **5**, 2845 (1972); **8**, 2591 (1975).

[20] See, for instance, G. Grosso and G. Pastori Parravicini, *Solid State Physics* (Academic Press, London, 2000) p. 185, and references quoted therein.

[21] J. C. Cullum and R. A. Willoughby, in *Lanczos Algorithms for Large Symmetric Eigenvalue Computations* (Birkhauser, Boston, 1985), Vols. I and II.

[22] B. R. Judd, in *The Dynamical Jahn-Teller effect in the Localized systems*, edited by Yu. E. Perlin and M. Wagner (North-Holland, Amsterdam, 1984).

[23] J.C. Slonczewski, Phys. Rev. **131**, 1596 (1963).

[24] J.A. Cina, T.J. Smith, Jr., and V. Romero-Rochin, Adv. Chem. Phys. **83**, 1 (1993); see also J. A. Cina, p. 117 in Ref. 4.

[25] J. Schön and H. Köppel, J. Chem. Phys. **103**, 9292 (1995).

[26] A. Kuppermann and Y.-S.M. Wu, Chem. Phys. Lett. **205**, 577 (1993).

[27] B.K. Kendrick, J. Chem. Phys. **112**, 5679 (2000).

[28] E. Wrede, L. Schnieder, K.H. Welge, F.J. Aoiz, L. Bañares, J.F. Castillo, B. Martínez-Haya, and V.J. Herrero, J. Chem. Phys. **110**, 9971 (1999).

[29] F. Fernández-Alonso, B.D. Bean, and R.N. Zare, J. Chem. Phys. **111**, 1022 (1999).