# The theory of double-beam three-photon absorption. II. Polarization ratio analysis

David L. Andrews

*School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England*
(Received 10 September 1982; accepted 5 November 1982)

This paper further develops the theory of double-beam three-photon spectroscopy introduced in part I. A much simpler method than that described previously is proposed for the experimental characterization of the three-photon excited states, where measurement of two polarization ratios alone suffices for a complete analysis. A comprehensive classification of the excited state symmetries is provided for the common molecular point groups.

## I. INTRODUCTION

In a recent paper,[1] henceforth denoted by I, it has been shown how the use of two laser sources in three-photon molecular spectroscopy provides access to a greater variety of excited states than if just one laser source is used. The transitions take place according to the energy relation

$$E_f = E_0 + \hbar\omega_1 + 2\hbar\omega_2 , \tag{1.1}$$

where one photon of frequency $\omega_1$ is absorbed from beam 1, and two photons of frequency $\omega_2$ are simultaneously absorbed from beam 2: the frequencies $\omega_1$ and $\omega_2$ necessarily differ for the purposes of this analysis. Compared with the process where three identical photons are absorbed from a single beam, much fuller symmetry information is provided by the double-beam experiment, thus removing some of the latent ambiguities in symmetry assignment.

In I, it was demonstrated that in a double-beam experiment with the beams crossed at 60°, the measurement of five spectra under different specified polarization conditions allows the determination of five molecular parameters which characterize the symmetry of the excited state, thereby providing for the unambiguous assignment of this excited state to one of six different symmetry classes.

Further study has now revealed that there is a much simpler method, involving the measurement of polarization ratios, for achieving the same objective. The measurement of polarization ratios is a well-established procedure in many areas of molecular spectroscopy; the widespread utilization of depolarization ratio data in Raman spectroscopy is probably the most familiar example. In the case of single-beam three-photon absorption, the ratio of the absorbance of circularly polarized light to that of plane polarized light is the most directly useful measurement, and has recently been discussed in detail by several authors.[2-4] In this paper, it is shown how the determination of just two polarization ratios in double-beam three-photon spectroscopy provides all the information required for a full analysis and classification of the excited state symmetry according to the principles developed previously.

## II. THEORY

The basic equations for the rate of three-photon absorption with arbitrary beam geometry and polarization have been derived in I. In these equations, each rate is expressed in terms of five distinct molecular parameters, based on a division of the molecular transition tensor $T_{\lambda\mu\nu}$ into irreducible parts, thus leading to a requirement for five separate experiments with different beam polarizations for a complete analysis. However, it may be shown that three of these rate equations are expressible in terms of just three molecular parameters which together completely determine the symmetry classification of the transition. These three parameters are products of the following irreducible tensors:

$$T^{(1C)}_{\lambda\mu\nu} = \tfrac{3}{10}(3\delta_{\lambda\mu}T_{\rho\rho\nu} + 3\delta_{\lambda\nu}T_{\rho\rho\mu} - 2\delta_{\mu\nu}T_{\rho\rho\lambda}) - \tfrac{1}{10}(4\delta_{\lambda\mu}T_{\nu\rho\rho} - \delta_{\lambda\nu}T_{\mu\rho\rho} - \delta_{\mu\nu}T_{\lambda\rho\rho}) , \tag{2.1}$$

$$T^{(2)}_{\lambda\mu\nu} = \tfrac{1}{6}\epsilon_{\lambda\mu\tau}(\epsilon_{\rho\sigma\tau}T_{\rho\sigma\nu} + \epsilon_{\rho\sigma\nu}T_{\rho\sigma\tau}) + \tfrac{1}{6}\epsilon_{\lambda\nu\tau}(\epsilon_{\rho\sigma\tau}T_{\rho\sigma\mu} + \epsilon_{\rho\sigma\mu}T_{\rho\sigma\tau}) , \tag{2.2}$$

$$T^{(3)}_{\lambda\mu\nu} = \tfrac{1}{3}(T_{\lambda\mu\nu} + T_{\mu\nu\lambda} + T_{\nu\lambda\mu}) - \tfrac{2}{15}(\delta_{\lambda\mu}T_{\rho\rho\nu} + \delta_{\lambda\nu}T_{\rho\rho\mu} + \delta_{\mu\nu}T_{\rho\rho\lambda}) - \tfrac{1}{15}(\delta_{\lambda\mu}T_{\nu\rho\rho} + \delta_{\lambda\nu}T_{\mu\rho\rho} + \delta_{\mu\nu}T_{\lambda\rho\rho}) . \tag{2.3}$$

In the above equations, the delta tensors are Kronecker deltas, the epsilons are Levi–Civita antisymmetric tensors, and the implied summation convention for repeated tensor indices is employed. Although the equation for $T^{(3)}_{\lambda\mu\nu}$ given here differs from that given in I, simple manipulation shows that the two expressions are exactly equivalent; details are given in the Appendix.

Each of the irreducible tensors defined by Eqs. (2.1) to (2.3) has different transformation properties under the operations of the rotation group: the weight 1 tensor $T^{(1C)}_{\lambda\mu\nu}$ transforms as a polar vector; $T^{(2)}_{\lambda\mu\nu}$ of weight 2 transforms as a traceless index-symmetric second rank axial tensor, and $T^{(3)}_{\lambda\mu\nu}$ of weight 3 transforms as a fully traceless and index-symmetric third rank polar tensor. Each tensor either has finite components or else is a null tensor according to the symmetry of the three-photon transition, as discussed in I. By methods described later, the particular combination of allowed tensor weights for a given transition can be determined, and hence the transition may be classified into one of the six symmetry classes introduced in I. A comprehensive list of the irreducible representations contained in each class is given for the common molecular point groups in Table I.

 0021-9606/83/041731-04$2.10  

TABLE I. Classification of three-photon excited state symmetries for the common molecular point groups.

| Class | IA | IB | IIA | IIB | III | IV |
|---|---|---|---|---|---|---|
| Weights | 1,2,3 | 1,3 | 2,3 | 3 | 1 | 2 |
| Nonaxial groups | | | | | | |
| $C_1$ | $A$ | ... | ... | ... | ... | ... |
| $C_i$ | $A_u$ | ... | ... | ... | ... | ... |
| $C_s$ | $A', A''$ | ... | ... | ... | ... | ... |
| Axial groups | | | | | | |
| $C_2$ | $A, B$ | ... | ... | ... | ... | ... |
| $C_3$ | $A, E$ | ... | ... | ... | ... | ... |
| $C_4$ | $A, E$ | ... | $B$ | ... | ... | ... |
| $C_5$ | $A, E_1$ | ... | $E_2$ | ... | ... | ... |
| $C_6$ | $A, E_1$ | ... | $E_2$ | $B$ | ... | ... |
| $S_4$ | $B, E$ | ... | $A$ | ... | ... | ... |
| $S_6$ | $A_u, E_u$ | ... | ... | ... | ... | ... |
| $S_8$ | $B, E_1$ | ... | $E_2$ | $E_3$ | ... | ... |
| $C_{2h}$ | $A_u, B_u$ | ... | ... | ... | ... | ... |
| $C_{3h}$ | $A'', E'$ | ... | $E''$ | $A'$ | ... | ... |
| $C_{4h}$ | $A_u, E_u$ | ... | $B_u$ | ... | ... | ... |
| $C_{5h}$ | $A'', E_1'$ | ... | $E_2''$ | $E_2'$ | ... | ... |
| $C_{6h}$ | $A_u, E_{1u}$ | ... | $E_{2u}$ | $B_u$ | ... | ... |
| $C_{2v}$ | $A_1, B_1, B_2$ | ... | $A_2$ | ... | ... | ... |
| $C_{3v}$ | $E$ | $A_1$ | $A_2$ | ... | ... | ... |
| $C_{4v}$ | $E$ | $A_1$ | $B_1, B_2$ | ... | ... | $A_2$ |
| $C_{5v}$ | $E_1$ | $A_1$ | $E_2$ | ... | ... | $A_2$ |
| $C_{6v}$ | $E_1$ | $A_1$ | $E_2$ | $B_1, B_2$ | ... | $A_2$ |
| Dihedral groups | | | | | | |
| $D_2$ | $B_1, B_2, B_3$ | ... | $A$ | ... | ... | ... |
| $D_3$ | $E$ | $A_2$ | $A_1$ | ... | ... | ... |
| $D_4$ | $E$ | $A_2$ | $B_1, B_2$ | ... | ... | $A_1$ |
| $D_5$ | $E_1$ | $A_2$ | $E_2$ | ... | ... | $A_1$ |
| $D_6$ | $E_1$ | $A_2$ | $E_2$ | $B_1, B_2$ | ... | $A_1$ |
| $D_{2h}$ | $B_{1u}, B_{2u}, B_{3u}$ | ... | $A_u$ | ... | ... | ... |
| $D_{3h}$ | $E'$ | $A_2''$ | $E''$ | $A_1', A_2'$ | ... | $A_1''$ |
| $D_{4h}$ | $E_u$ | $A_{2u}$ | $B_{1u}, B_{2u}$ | ... | ... | $A_{1u}$ |
| $D_{5h}$ | $E_1'$ | $A_2''$ | $E_2''$ | $E_2'$ | ... | $A_1''$ |
| $D_{6h}$ | $E_{1u}$ | $A_{2u}$ | $E_{2u}$ | $B_{1u}, B_{2u}$ | ... | $A_{1u}$ |
| $D_{2d}$ | $E$ | $B_2$ | $A_1, A_2$ | ... | ... | $B_1$ |
| $D_{3d}$ | $E_u$ | $A_{2u}$ | $A_{1u}$ | ... | ... | ... |
| $D_{4d}$ | $E_1$ | $B_2$ | $E_2$ | $E_3$ | ... | $B_1$ |
| $D_{5d}$ | $E_{1u}$ | $A_{2u}$ | $E_{2u}$ | ... | ... | $A_{1u}$ |
| $D_{6d}$ | $E_1$ | $B_2$ | $E_4$ | $E_3$ | ... | $B_1$ |
| Linear groups | | | | | | |
| $C_{\infty v}$ | $\Pi$ | $\Sigma^+$ | $\Delta$ | $\Phi$ | ... | $\Sigma^-$ |
| $D_{\infty h}$ | $\Pi_u$ | $\Sigma_u^+$ | $\Delta_u$ | $\Phi_u$ | ... | $\Sigma_u^-$ |
| Cubic groups | | | | | | |
| $T$ | $T$ | ... | ... | $A$ | ... | $E$ |
| $T_h$ | $T_u$ | ... | ... | $A_u$ | ... | $E_u$ |
| $T_d$ | ... | $T_2$ | $T_1$ | $A_1$ | ... | $E$ |
| $O$ | ... | $T_1$ | $T_2$ | $A_2$ | ... | $E$ |
| $O_h$ | ... | $T_{1u}$ | $T_{2u}$ | $A_{2u}$ | ... | $E_u$ |
| Icosahedral groups | | | | | | |
| $I$ | ... | ... | ... | $T_2, G$ | $T_1$ | $H$ |
| $I_h$ | ... | ... | ... | $T_{2u}, G_u$ | $T_{1u}$ | $H_u$ |

We can now consider the rate equations for three specific experimental arrangements. *In each case, beam 2 is circularly polarized, and the angle between the two beams is* 60°. (It is readily established that for beam angles of 0°, 90°, or 180°, the corresponding equations are no longer linearly independent, and hence the analysis is incomplete without further polarization measurements.) The three experiments are as follows:

TABLE II. Values of the polarization ratios $\alpha$ and $\beta$ for transitions belonging to each symmetry class.

| Class | IA | IB | IIA | IIB | III | IV |
|---|---|---|---|---|---|---|
| Weights | 1, 2, 3 | 1, 3 | 2, 3 | 3 | 1 | 2 |
| Polarization ratios | $\frac{8}{13} < \alpha < 8$ | $\frac{64}{83} < \alpha < 8$ | $\frac{8}{13} < \alpha < \frac{64}{83}$ | $\alpha = \frac{64}{83}$ | $\alpha = 8$ | $\alpha = \frac{8}{13}$ |
| | $\frac{46}{83} < \beta < 2$ | $\beta = \frac{(\alpha+2)}{5}$ | $\beta = \frac{(54-65\alpha)}{7}$ | $\beta = \frac{46}{83}$ | $\beta = 2$ | $\beta = 2$ |

(i) Beam 1 is plane polarized with its electric field vector perpendicular to the plane containing the two beams. The rate of absorption, denoted here by $\Gamma_\perp$, corresponds to $\Gamma_3'$ in I.

(ii) Beam 1 is plane polarized with its electric field vector lying in the plane containing the two beams. The rate of absorption is denoted by $\Gamma_\parallel$, and corresponds to $\Gamma_4'$ in I.

(iii) Beam 1 is circularly polarized with the same helicity as beam 2, and the rate here denoted by $\Gamma_C$ corresponds to $\Gamma_5'$ in I.

In terms of the irreducible tensors given by Eqs. (2.1) to (2.3), the three rate equations are as follows:

$$\Gamma_\perp = \frac{G}{1050}\left(7T^{(1C)}_{\lambda\lambda\mu}\bar{T}^{(1C)}_{\nu\nu\mu} + 35T^{(2)}_{\lambda\mu\nu}\bar{T}^{(2)}_{\lambda\mu\nu} + 80T^{(3)}_{\lambda\mu\nu}\bar{T}^{(3)}_{\lambda\mu\nu}\right), \tag{2.4}$$

$$\Gamma_\parallel = \frac{G}{4200}\left(7T^{(1C)}_{\lambda\lambda\mu}\bar{T}^{(1C)}_{\nu\nu\mu} + 455T^{(2)}_{\lambda\mu\nu}\bar{T}^{(2)}_{\lambda\mu\nu} + 230T^{(3)}_{\lambda\mu\nu}\bar{T}^{(3)}_{\lambda\mu\nu}\right), \tag{2.5}$$

$$\Gamma_C = \frac{G}{8400}\left(7T^{(1C)}_{\lambda\lambda\mu}\bar{T}^{(1C)}_{\nu\nu\mu} + 455T^{(2)}_{\lambda\mu\nu}\bar{T}^{(2)}_{\lambda\mu\nu} + 830T^{(3)}_{\lambda\mu\nu}\bar{T}^{(3)}_{\lambda\mu\nu}\right), \tag{2.6}$$

where $G$ is an absorption constant which is independent of the beam angle or polarizations, and is defined in I. The above equations can be solved for the three molecular parameters to give the results

$$T^{(1C)}_{\lambda\lambda\mu}\bar{T}^{(1C)}_{\nu\nu\mu} = \tfrac{5}{2}G^{-1}(65\Gamma_\perp + 7\Gamma_\parallel - 54\Gamma_C), \tag{2.7}$$

$$T^{(2)}_{\lambda\mu\nu}\bar{T}^{(2)}_{\lambda\mu\nu} = \tfrac{5}{2}G^{-1}(5\Gamma_\parallel - \Gamma_\perp - 2\Gamma_C), \tag{2.8}$$

$$T^{(3)}_{\lambda\mu\nu}\bar{T}^{(3)}_{\lambda\mu\nu} = 7G^{-1}(2\Gamma_C - \Gamma_\parallel). \tag{2.9}$$

The zero or nonzero values of each weight of the molecular transition tensor can thus be established from these three experiments. However, a much more direct method involving the study of polarization ratios is demonstrated below.

## III. POLARIZATION RATIOS

We now introduce polarization ratios, defined as ratios of the absorbance of plane polarized light to that of circularly polarized light. In the double-beam three-photon experiment we have considered, where beam 2 is taken to have circular polarization in every case, we may take ratios of the three-photon absorbance dependent upon the polarization of beam 1. Since we have two orthogonal planes of polarization for beam 1, there are two such ratios to consider, and these are defined by

$$\alpha = \Gamma_\perp/\Gamma_C, \tag{3.1}$$

$$\beta = \Gamma_\parallel/\Gamma_C. \tag{3.2}$$

The values of $\alpha$ and $\beta$ depend entirely on the symmetry of the three-photon excited state, and they provide a means for discriminating between the six symmetry classes described in I; the results are tabulated for each class in Table II. (Here we assume that the incident light frequencies are sufficiently far removed from resonances with intermediate states that the imaginary part of each $T_{\lambda\mu\nu}$ element is smaller than the real part, so that each of the three molecular parameters $T^{(1C)}_{\lambda\lambda\mu}\times\bar{T}^{(1C)}_{\nu\nu\mu}$, $T^{(2)}_{\lambda\mu\nu}\bar{T}^{(2)}_{\lambda\mu\nu}$, and $T^{(3)}_{\lambda\mu\nu}\bar{T}^{(3)}_{\lambda\mu\nu}$ is both real and positive.) Note that $\alpha$ and $\beta$ are only genuinely independent for a Class IA transition.

The simplest way to assign a three-photon transition to one of the six classes is then by a diagrammatic method illustrated in Fig. 1. Figure 1(a) shows the result of plotting the values of the polarization ratio $\beta$

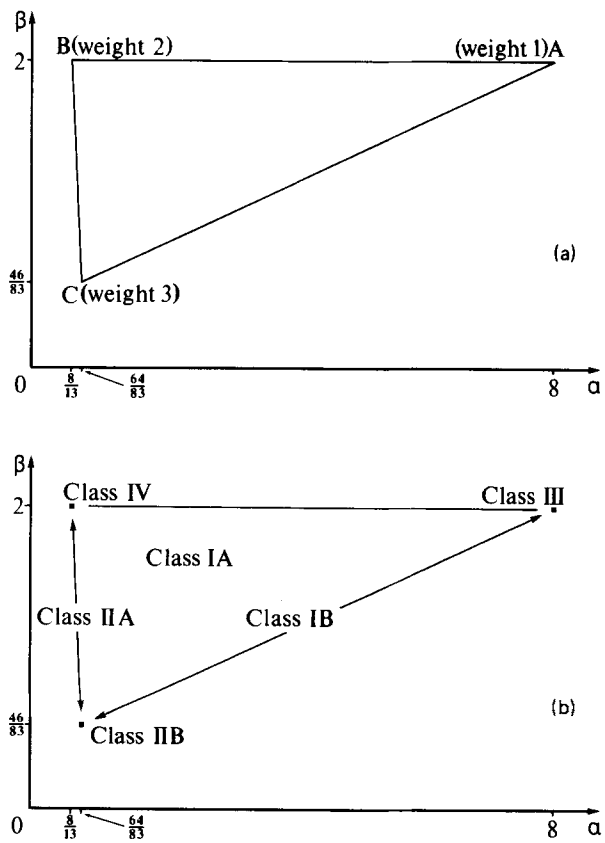


FIG. 1. Symmetry assignment of three-photon transitions on the basis of polarization ratios $\alpha$ and $\beta$.

against the values of $\alpha$. For any three-photon transition, the point $(\alpha,\beta)$ representing the results of the two polarization ratio measurements must lie within the triangle ABC having vertices $(8,2)$, $(\frac{8}{13},2)$, and $(\frac{64}{83},\frac{46}{83})$. These vertices may be associated with weights 1, 2, and 3, respectively, as indicated on the diagram; experimental results may then be interpreted as follows.

If $(\alpha,\beta)$ lies at one of the vertices $A$, $B$, or $C$, then $T_{\lambda\mu\nu}$ contains contributions of one weight only, i.e., weight 1, 2, or 3, respectively; hence the transition belongs to Class III, IV, or II B respectively. If $(\alpha,\beta)$ lies on the line AC, then $T_{\lambda\mu\nu}$ contains weights 1 and 3, and hence the transition belongs to Class I B; if $(\alpha,\beta)$ lies on the line BC, then $T_{\lambda\mu\nu}$ contains weights 2 and 3, and the transition belongs to Class II A. Finally, if $(\alpha,\beta)$ lies anywhere else within ABC, then the molecular transition tensor contains all three weights, and thus the transition belongs to Class I A. The results are illustrated in Fig. 1(b).

## IV. CONCLUSION

It has been shown how double-beam three-photon absorption experiments with three different polarizations of one beam provide all the information necessary for a complete symmetry analysis of each excited state. By ratioing the spectra obtained under these conditions, two polarization ratios $\alpha$ and $\beta$ are obtained for each transition, and by reference to the simple diagram shown in Fig. 1(b), an immediate classification can be made according to the sixfold symmetry classification scheme developed in I. By reference to Table I, it should then be possible to completely determine the irreducible representation of most three-photon excited states. This is a considerable simplification of the method proposed previously.

## APPENDIX

The expression for $T^{(3)}_{\lambda\mu\nu}$ given in Eq. (2.3) differs from that given in I: in this Appendix, it is demonstrated that the two results are exactly equivalent. The equation for $T^{(3)}_{\lambda\mu\nu}$ in I is as follows:

$$\begin{aligned} T^{(3)}_{\lambda\mu\nu} &= T_{\lambda\mu\nu} - T^{(1A)}_{\lambda\mu\nu} - T^{(1B)}_{\lambda\mu\nu} - T^{(2)}_{\lambda\mu\nu} \\ &= T_{\lambda\mu\nu} - \tfrac{1}{10}(3\delta_{\lambda\mu}T_{\rho\rho\nu} + 3\delta_{\lambda\nu}T_{\rho\rho\mu} - 2\delta_{\mu\nu}T_{\rho\rho\lambda}) - \tfrac{1}{10}(-\delta_{\lambda\mu}T_{\nu\rho\rho} - \delta_{\lambda\nu}T_{\mu\rho\rho} + 4\delta_{\mu\nu}T_{\lambda\rho\rho}) - \tfrac{1}{6}[\epsilon_{\lambda\mu\tau}(\epsilon_{\rho\sigma\tau}T_{\rho\sigma\nu} + \epsilon_{\rho\sigma\nu}T_{\rho\sigma\tau}) \\ &\quad + \epsilon_{\lambda\nu\tau}(\epsilon_{\rho\sigma\tau}T_{\rho\sigma\mu} + \epsilon_{\rho\sigma\mu}T_{\rho\sigma\tau})]\,. \end{aligned} \tag{A1}$$

The last four terms in Eq. (A1) which involve products of Levi–Civita antisymmetric tensors may be expanded using the following well-known results:

$$\epsilon_{\lambda\mu\tau}\epsilon_{\rho\sigma\nu} = \begin{vmatrix} \delta_{\lambda\rho} & \delta_{\lambda\sigma} & \delta_{\lambda\nu} \\ \delta_{\mu\rho} & \delta_{\mu\sigma} & \delta_{\mu\nu} \\ \delta_{\tau\rho} & \delta_{\tau\sigma} & \delta_{\tau\nu} \end{vmatrix}, \tag{A2}$$

$$\epsilon_{\lambda\mu\tau}\epsilon_{\rho\sigma\tau} = \delta_{\lambda\rho}\delta_{\mu\sigma} - \delta_{\lambda\sigma}\delta_{\mu\rho}\,. \tag{A3}$$

Hence, we obtain

$$\begin{aligned} T^{(3)}_{\lambda\mu\nu} &= T_{\lambda\mu\nu} - \tfrac{1}{10}(3\delta_{\lambda\mu}T_{\rho\rho\nu} + 3\delta_{\lambda\nu}T_{\rho\rho\mu} - 2\delta_{\mu\nu}T_{\rho\rho\lambda}) - \tfrac{1}{10}(-\delta_{\lambda\mu}T_{\nu\rho\rho} - \delta_{\lambda\nu}T_{\mu\rho\rho} + 4\delta_{\mu\nu}T_{\lambda\rho\rho}) - \tfrac{1}{6}[T_{\lambda\mu\nu} - T_{\mu\lambda\nu} + T_{\lambda\mu\nu} - T_{\lambda\tau\tau}\delta_{\mu\nu} \\ &\quad - T_{\mu\lambda\nu} + T_{\tau\lambda\tau}\delta_{\mu\nu} + T_{\mu\tau\tau}\delta_{\lambda\nu} - T_{\tau\mu\tau}\delta_{\lambda\nu} + T_{\lambda\nu\mu} - T_{\nu\lambda\mu} + T_{\lambda\nu\mu} - T_{\lambda\tau\tau}\delta_{\mu\nu} - T_{\nu\lambda\mu} + T_{\tau\lambda\tau}\delta_{\mu\nu} + T_{\nu\tau\tau}\delta_{\lambda\mu} - T_{\tau\nu\tau}\delta_{\lambda\mu}]\,. \end{aligned} \tag{A4}$$

By replacing the dummy index $\tau$ by $\rho$ and making use of the index symmetry in the last two indices of $T_{\lambda\mu\nu}$, we then obtain the expression for $T^{(3)}_{\lambda\mu\nu}$ exactly as given in Eq. (2.3).

[1]D. L. Andrews, J. Chem. Phys. 77, 2831 (1982).
[2]D. L. Andrews and W. A. Ghoul, J. Chem. Phys. 75, 530 (1981).
[3]G. C. Nieman, J. Chem. Phys. 75, 584 (1981).
[4]D. M. Friedrich, J. Chem. Phys. 75, 3258 (1981).