DOPPLER-FREE MULTIPHOTON ABSORPTION IN ICOSAHEDRAL MOLECULES

David L. ANDREWS and Kevin P. HOPKINS
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

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It is shown that with counter-propagating laser beams of identical circular polarisation, symmetry-preserving transitions in icosahedral molecules produce *totally* Doppler-free lines in two-photon and four-photon absorption spectra. In the four-photon case, this feature cannot occur for molecules of any other symmetry, and therefore characterises an icosahedral species.

1. Introduction

Until recently the chemical physics of icosahedral species was a matter of largely academic interest, since only the borohydride anion $B_{12}H_{12}^{2-}$ was known to have this structure. However, with the synthesis [1] of dodecahedrane, $C_{20}H_{20}$, and the characterisation [2] of Buckminsterfullerene, C_{60}, there is now a new significance to the study of icosahedral compounds in the gas phase. In the more widely studied case of C_{60}, there are two possible structures [3], but icosahedral symmetry has been positively confirmed by the study of various spectroscopic properties (see for example refs. [4–7]), and also by recent X-ray cyrstallographic measurements [8]. Alongside the experimental work, there has been renewed theoretical interest in the electronic, vibrational, and rotational states of such compounds [9–23].

It is the purpose of this paper to draw attention to a novel feature predicted by theory in the multiphoton spectroscopy of such species. Doppler-free multiphoton absorption spectroscopy is based on a first-order cancellation of Doppler frequency shifts. This is accomplished by arranging that the wave-vectors of the absorbed photons give a vector sum of zero [24]. This paper is concerned with two simple cases; (i) the two-photon absorption of counter-propagating photons of equal frequency, and (ii) the four-photon absorption of two pairs of counter-propagating photons. In both cases it is shown that the use of circularly polarised light produces a feature which characterises icosahedral symmetry.

2. Two-photon absorption

We begin by reviewing the irreducible tensor calculus for the simpler case of two-photon absorption. The rate of absorption, obtained by means of the standard methods of quantum electrodynamics [25], can be expressed in the form

$$\Gamma = K_2 \, | e_{1i} e_{2j} T_{ij} |^2 \, . \tag{1}$$

Here $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are the polarisation vectors of the two absorbed photons, $\mathbf{T}$ is the two-photon molecular response tensor for the transition, and there is implied summation over the repeated indices $i, j = (x, y, z)$. The symmetry analysis of the above expression is facilitated by recasting both the "polarisation tensor" $(e_{1i}e_{2j})$ and the molecular tensor in irreducible form.

The decomposition of a general, reducible, second-rank Cartesian tensor S_{ij}, into irreducible parts takes the form [25]

$$S_{ij} = S_{ij}^{(0)} + S_{ij}^{(1)} + S_{ij}^{(2)} \, . \tag{2}$$

Here, $S_{ij}^{(0)}$ is a weight-0 tensor which transforms under the operations of the full rotation group as a scalar; $S_{ij}^{(1)}$ is a weight-1 tensor, which transforms as a pseudo-vector (i.e. its components have the same transformation properties as the rotations, R_x, R_y, R_z); and $S_{ij}^{(2)}$ is a weight-2 tensor which transforms as a second-rank, symmetric, traceless tensor (i.e. its components transform in the same way as xy, xz, yz, x^2-y^2 and $2z^2-x^2-y^2$).

Since index-symmetry properties dictate that the inner product of two irreducible tensors of the same

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rank but different weight is zero, the cross-terms in eq. (1) vanish and we have

$$\Gamma = K_2 \,|\, (e_{1i}e_{2j})^{(0)} T_{ij}^{(0)} + (e_{1i}e_{2j})^{(1)} T_{ij}^{(1)} + (e_{1i}e_{2j})^{(2)} T_{ij}^{(2)} \,|^2 . \quad (3)$$

If a particular molecular transition is to be observed, it is necessary that one or more of the irreducible molecular tensors transforms under the same irreducible representation as the transition. In particular, a symmetry-preserving two-photon transition in a cubic or icosahedral species (in which the product of the initial and final states is spanned by the A_{1g} irreducible representation in O_h, or the A_g irreducible representation in I_h), will only be observed in the spectrum if the corresponding weight-0 contributions to the rate equation are non-zero. (In molecules of any other symmetry, weight-2 contributions also transform under the totally symmetric representation, and therefore the absence of a weight-0 term does *not* necessarily imply that the transition is forbidden.)

The explicit form of each irreducible tensor contribution is obtained through use of the relations

$$T_{ij}^{(0)} = \tfrac{1}{3}\delta_{ij} T_{kk} , \quad (4)$$

$$T_{ij}^{(1)} = \tfrac{1}{2}(T_{ij} - T_{ji}) , \quad (5)$$

$$T_{ij}^{(2)} = \tfrac{1}{2}(T_{ij} + T_{ji}) - \tfrac{1}{3}\delta_{ij} T_{kk} , \quad (6)$$

$$(e_{1i}e_{2j})^{(0)} = \tfrac{1}{3}\delta_{ij}(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2) , \quad (7)$$

$$(e_{1i}e_{2j})^{(1)} = \tfrac{1}{2}[(e_{1i}e_{2j}) - (e_{1j}e_{2i})] , \quad (8)$$

$$(e_{1i}e_{2j})^{(2)} = \tfrac{1}{2}[(e_{1i}e_{2j}) + (e_{1j}e_{2i})] - \tfrac{1}{3}\delta_{ij}(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2) . \quad (9)$$

Since the *molecular* tensor is index-symmetric if the two absorbed photons are of the same frequency, $T_{ij}^{(1)}$ vanishes and there is *no weight*-1 contribution to the process. Clearly, the presence or absence of the *weight*-0 component depends on the value of the dot product $(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)$.

With counter-propagating plane polarised beams the value of the dot product $(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)$ is determined by the angle between the two polarisation vectors. In the particular case where both photons are derived from a single beam, the dot product must always have the value of unity. Hence the rate equation for a symmetry-preserving transition will always contain a weight-0 contribution arising from the absorption of two photons from the same beam. Thus whilst the absorption of two *counter-propagating* photons will indeed produce a Doppler-free signal, the overall absorption profile will be one in which this Doppler-free line is superimposed on a band which carries the usual Doppler broadening. Special features arise with circularly polarised radiation, however, and we therefore concentrate on this case below.

When two counter-propagating circularly polarised laser beams are employed, $(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)$ is zero if both photons are derived from the same beam, since $e^{(L/R)} = (1/\sqrt{2})(\hat{\imath} \pm i\hat{\jmath})$. The absorption of two co-propagating photons therefore *cannot* induce a symmetry-preserving transition in O_h or I_h molecules: hence there is no Doppler-broadened background for such transitions (see table 1). A physical explanation for this behaviour lies in the fact that any two co-propagating circularly polarised photons carry a net spin angular momentum of $2\hbar$, and thus can only be absorbed in two-photon transitions which result in the transfer of this angular momentum to the absorber. Symmetry-preserving transitions (i.e. transitions of weight-0 character) in molecules of cubic or icosahedral symmetry can, however, only occur if there is no net uptake of angular momentum, and thus can only be induced by the absorption of *counter*-propagating photons. For the case where the beams are circularly polarised with *opposite* helicity, there is also no weight-0 contribution to $(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)$, from counter-propagating photons since a left-circularly polarised photon moving from left to right has the same polarisation vector as a right-circularly polarised photon moving from right to left, and vice versa. Hence symmetry-preserving transitions are in this case entirely forbidden.

However with counter-propagating beams of the *same* handedness, a weight-0 contribution from $(\boldsymbol{e}_1 \cdot \boldsymbol{e}_2)$ *is* observed when one photon is derived from each beam: thus whilst the absorption of two photons from either beam, i.e. co-propagating photons, is a forbidden process, the absorption of counter-propagating photons is allowed. Hence under this particular experimental arrangement, a Doppler-free absorption band occurs in the two-photon spectrum *without* the normal Doppler-broadened background. This is the only experimental configuration whereby a totally symmetric transition in these point groups can produce a Doppler-free peak in the two-photon absorption spectrum: the effect thus characterises

Table 1
Form of $S_{ij}^{(0)}$ and $(e_1 \cdot e_2)$ for all possible cases of two-photon absorption with counter-propagating circularly polarised beams: e_1 and e_2 denote the polarisation vectors of the two absorbed photons, whilst e and e' denote the polarisations of the two beams. A weight-0 transition is only allowed when $(e_1 \cdot e_2) \neq 0$

	Form of $S_{ij}^{(0)}$	$(e_1 \cdot e_2)$
counter-propagating beams of the *same* helicity		
two photons absorbed from the same beam	$(e_{1i}e_{2j})^{(0)}$	0
	$(e'_{1i}e'_{2j})^{(0)}$	0
one photon absorbed from each beam	$(e_{1i}e'_{2j})^{(0)}$	1
counter-propagating beams of *opposite* helicity		
two photons absorbed from the same beam	$(e_{1i}e_{2j})^{(0)}$	0
	$(e'_{1i}e'_{2j})^{(0)}$	0
one photon absorbed from each beam	$(e_{1i}e'_{2j})^{(0)}$	0

either cubic or icosahedral symmetry. A similar effect is a well-known feature of Doppler-free *atomic* spectroscopy [24].

3. Four-photon absorption

Whilst there is no analogue to this behaviour in three-photon absorption, similar remarks can be made concerning the four-photon case. The rate of four-photon absorption can be expressed as

$$\Gamma = K_4 \, | e_{1i} e_{2j} e_{3k} e_{4l} T_{ijkl} |^2 , \qquad (10)$$

where e_1, e_2, e_3 and e_4 are the polarisation vectors of the four absorbed photons, and T_{ijkl} is the four-photon molecular response tensor for the transition. The weight-0 contribution to the overall rate then arises from

$$\Gamma^{(0)} = K_4 \, | (e_{1i} e_{2j} e_{3k} e_{4l})^{(0)} T_{ijkl}^{(0)} |^2 , \qquad (11)$$

where the explicit forms of the irreducible tensors are given by [26]

$$T_{ijkl}^{(0)} = \begin{bmatrix} \delta_{ij}\delta_{kl} \\ \delta_{ik}\delta_{jl} \\ \delta_{il}\delta_{jk} \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} T_{mmnn} \\ T_{mnmn} \\ T_{mnnm} \end{bmatrix} \qquad (12)$$

and

$$(e_{1i} e_{2j} e_{3k} e_{4l})^{(0)} = \begin{bmatrix} \delta_{ij}\delta_{kl} \\ \delta_{ik}\delta_{jl} \\ \delta_{il}\delta_{jk} \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} (e_1 \cdot e_2)(e_3 \cdot e_4) \\ (e_1 \cdot e_3)(e_2 \cdot e_4) \\ (e_1 \cdot e_4)(e_2 \cdot e_3) \end{bmatrix} . \qquad (13)$$

The presence, or absence, of a weight-0 contribution to the spectrum thus depends on a non-zero value for at least one of the terms in the right-hand bracket of eq. (13). The values of these terms for a number of combinations of beam polarisations are presented in table 2. As in the case of two-photon absorption, employing counter-propagating beams of opposite helicity produces no weight-0 contribution. With two counter-propagating circularly polarised beams of the *same* handedness, the only allowed mechanism for a four-photon symmetry-preserving transition involves absorbing a pair of photons from each beam. Once again this results in each such transition producing a Doppler-free line in the spectrum. However, in this case the effect is limited to icosahedral species: in molecules of any other symmetry, there are no cases where a weight-0 contribution arises without other weights being simultaneously represented [27].

Our results show that in an experiment based on counter-propagating laser beams of identical frequency and circular polarisations, an *entirely* Doppler-free line in a four-photon absorption spectrum should unambiguously signify icosahedral symmetry. A note of caution needs to be sounded on two points, however. First, we note that in a particular molecule certain four-photon transitions may involve additional tensor contributions of weight 2 or 4 which, although allowed, may be weak compared to the weight-0 contribution. This could produce a false positive result with the appearance of an essentially Doppler-free line which would normally characterise a pure weight-0 transition. This problem might be overcome by confirming that the line

Table 2
Form of $S^{(0)}_{ijkl}$ and the three quantities $A=(e_1\cdot e_2)(e_3\cdot e_4)$, $B=(e_1\cdot e_3)(e_2\cdot e_4)$ and $C=(e_1\cdot e_4)(e_2\cdot e_3)$, for all possible cases of four-photon absorption with counter-propagating circularly polarised beams: e_1, e_2, e_3 and e_4 denote the polarisation vectors of the four absorbed photons, whilst e and e' denote the polarisations of the two beams. A weight-0 transition is only allowed if A, B or $C\neq 0$

	Form of $S^{(0)}_{ijkl}$	A	B	C
counter-propagating beams of the *same* helicity				
four photons absorbed from one beam	$(e_{1i}e_{2j}e_{3k}e_{4l})^{(0)}$	0	0	0
	$(e'_{1i}e'_{2j}e'_{3k}e'_{4l})^{(0)}$	0	0	0
three photons absorbed from one beam	$(e_{1i}e_{2j}e_{3k}e'_{4l})^{(0)}$	0	0	0
	$(e'_{1i}e'_{2j}e'_{3k}e_{4l})^{(0)}$	0	0	0
two photons absorbed from each beam	$(e_{1i}e_{2j}e'_{3k}e'_{4l})^{(0)}$	0	1	1
counter-propagating beams of *opposite* helicity				
any combination	any	0	0	0

disappears when a *single* circularly polarised laser beam is used for the excitation (since, as table 2 shows, the weight-0 term for a symmetry-preserving transition then disappears). Secondly, the need to distinguish Doppler-free lines with and without Doppler-broadened background might prove experimentally difficult. However, we are confident that the considerable ingenuity of the spectroscopists involved in this field can be successfully brought to bear on the problem.

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References

[1] L.A. Paquette, R.J. Ternansky, D.W. Balough and G. Kentagen, J. Am. Chem. Soc. 105 (1983) 5446.
[2] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, Nature 318 (1985) 162.
[3] T.I. Shibuya and M. Yoshitani, Chem. Phys. Letters 137 (1987) 13.
[4] E.A. Rohlfing, D.M. Cox and A. Kaldor, J. Chem. Phys. 81 (1984) 3322.
[5] S.H. Yang, C.L. Pettiette, J. Conceicao, O. Cheshnovsky and R.E. Smalley, Chem. Phys. Letters 139 (1987) 233.
[6] J.R. Heath, R.F. Curl and R.E. Smalley, J. Chem. Phys. 87 (1987) 4236.
[7] I. László and L. Udvardi, Chem. Phys. Letters 136 (1987) 418.
[8] S. Iijima, J. Phys. Chem. 91 (1987) 3466.
[9] R.A. Davidson, Theoret. Chim. Acta 58 (1981) 193.
[10] W.G. Harter and D.E. Weeks, Chem. Phys. Letters 132 (1986) 387.
[11] D.S. Marynick and S. Estreicher, Chem. Phys. Letters 132 (1986) 383.
[12] D.J. Klein, T.G. Schmalz, G.E. Hite and W.A. Seitz, J. Am. Chem. Soc. 108 (1986) 1301.
[13] R.C. Haddon, L.E. Brus and K. Raghavachari, Chem. Phys. Letters 125 (1986) 459.
[14] M.D. Newton and R.E. Stanton, J. Am. Chem. Soc. 108 (1986) 2469.
[15] A.D.J. Haymet, J. Am. Chem. Soc. 108 (1986) 319.
[16] R.L. Disch and J.M. Schulman, Chem. Phys. Letters 125 (1986) 465.
[17] K.E. Schriver, A.J. Paguia, M.Y. Hahn, E.C. Honea, A.M. Camarena and R.L. Whetten, J. Phys. Chem. 91 (1987) 3131.
[18] B.W. van de Waal, J. Chem. Phys. 86 (1987) 5660.
[19] S. Larsson, A. Volosov and A. Rosén, Chem. Phys. Letters 137 (1987) 501.
[20] H.P. Lüthi and J. Almlöf, Chem. Phys. Letters 135 (1987) 357.
[21] J.R. Heath, S.C. O'Brien, R.F. Curl, H.W. Kroto and R.E. Smalley, Comments Condensed Matter Phys. 13 (1987) 119.
[22] Z.C. Wu, D.A. Jelski and T.F. George, Chem. Phys. Letters 137 (1987) 291.
[23] S.J. Cyvin, E. Brendsdal, B.N. Cyvin and J. Brunvoll, Chem. Phys. Letters 143 (1988) 377.
[24] M.D. Levenson, Introduction to nonlinear spectroscopy (Academic Press, New York, 1982).
[25] D.P. Craig and T. Thirunamachandran, Molecular quantum electrodynamics (Academic Press, New York, 1984).
[26] D.L. Andrews and W.A. Ghoul, Phys. Rev. A 25 (1982) 2647.
[27] D.L. Andrews and W.A. Ghoul, J. Chem. Phys. 75 (1981) 530.